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Document Number 33

Entry 33 of 240

File: USPT

Apr 20, 1999

DOCUMENT-IDENTIFIER: US 5895509 A

TITLE: Abrasive composition

ABPL:

An abrasive composition which can realize chemical-mechanical polishing superior in polishing speed and polishing uniformity.

ABPL:

S702
CE

The abrasive composition comprises abrasive grains, isopropyl alcohol, and water. Grain sizes of the abrasive grains are preferably 30 to 350 nm, and the abrasive grains are preferably SiO₂. Further, it is preferable that contents of the abrasive grains and isopropyl alcohol are 5 to 30 wt % and 1 to 15 wt %, respectively. The abrasive composition of the present invention is characterized in that it is deaerated.

BSPR:

no O₂

The present invention relates to an abrasive composition, and in particular to an abrasive composition used in chemical-mechanical polishing for a semiconductor surface in a semiconductor manufacturing process.

BSPR:

In conventional chemical-mechanical polishing, planarization polishing of inter layer insulating film is performed with an abrasive composition consisting of silica dispersed in water, and employing an apparatus such as shown in FIG. 6. In FIG. 6, 601 refers to a wafer, which is mounted on a wafer support 602 which turns on its axis, revolves, and swings left, right, back and forth, with the wafer's surface to be polished being directed downward. A reference number 603 refers to an abrasive composition supply pipe for dropping an abrasive composition. By 604, is referred to a polishing pad mounted on a rotating pad support 605.

BSPR:

The abrasive composition is dropped onto the polishing pad 604 through the supply pipe 603. Relative movement between the wafer 601 and the pad 604 makes the dropped abrasive composition enter between the wafer 601 and the pad 604, thus the inter layer insulating film of the wafer 601 is polished by sliding on and being rubbed by the pad 604.

BSPR:

According to this conventional polishing method, however, it is difficult to supply the abrasive on a wafer surface entirely and uniformly, and its polishing uniformity is poor.

BSPR:

As a method to solve the problem, there has been studied a method in which holes are provided in a polishing pad and an abrasive composition is supplied through those holes, which increased uniformity in supplying an abrasive composition onto a wafer surface. However, the obtained uniformity in polishing is not sufficient, and its reproducibility is poor.

BSPR:

The present inventor has studied the cause of low polishing uniformity from both the viewpoint of polishing methods and abrasive compositions, to find that polishing uniformity is greatly affected by composition of an abrasive composition and static electrification properties of a polishing pad and the abrasive composition. The present invention has been completed, based on those findings.

BSPR:

The abrasive composition of the present invention is characterized in that it comprises abrasive grains, isopropyl alcohol, and water.

BSPR:

Preferably, the size of the abrasive grains is 30 to 250 nm in their diameter. It is also preferable that the abrasive grains is $\text{SiO}_{\text{sub.}2}$.

BSPR:

Preferably also, contents of the abrasive grains and isopropyl alcohol are 5 to 30 wt % and 1 to 15 wt %, respectively.

BSPR:

Further, the abrasive composition according to the invention is characterized in that it has been deaerated.

DRPR:

FIG. 1 is a conceptual view showing an example of a polishing apparatus with which the abrasive composition of the present invention is preferably applied;

DRPR:

FIG. 2 is a conceptual view showing an example of an arrangement of holes provided in a pad for supplying the abrasive composition;

DRPR:

FIGS. 3(a) and 3(b) are graphs showing polished results over a surface of a pad by the abrasive composition of the present invention and by the conventional abrasive composition: FIG. 3(a) showing the conventional case, and FIG. 3(b) the present invention;

DRPR:

FIG. 4 is a graph showing static electrification properties of the abrasive composition and file pad;

DRPR:

FIG. 5 is a graph showing a relation between content of isopropyl alcohol and mean polishing speed; and

DEPR:

The abrasive composition according to the present invention is obtained by dispersing abrasive grains into water if needed, potassium hydroxide or the like may be added to make it alkaline and to improve aggregation-prevention), and by adding, little by little, a mixture consisting of isopropyl alcohol and water. Using the abrasive composition of the present invention, polishing speed and uniformity are improved.

DEPR:

In the present invention, as the abrasive grains, there may be used an inorganic abrasive grains such as an oxide, for example, silica, ceria ($\text{CeO}_{\text{sub.}2}$), or the like, as well as organic resin type abrasive grains. When used for super fine polishing of semiconductor surface, such as inter layer insulating an formed on a surface of semiconductor for multilayered wiring it is preferable to use abrasive grains of oxide type, in particular, silica.

DEPR:

As for grain diameter of the abrasive grains, 30 to 250 nm is preferable. Using grains having diameters within this range, there is

obtained high polishing speed and polishing uniformity. Grain diameters less than 30 nm decreases polishing speed, while, if it is more than 250 nm, polishing uniformity is decreased and, sometimes, the semiconductor surface is damaged.

DEPR:

Preferably, contents of the abrasive grains is 5 to 30 wt %. When it is less than 5 wt %, polishing speed is lowered, and when it is more than 30 wt %, the degree of dispersion is lowered to produce aggregations and to decrease polishing uniformity.

DEPR:

Mixing of isopropyl alcohol in the abrasive composition has an effect of spreading the abrasive grains over the pad surface, thus improving polishing uniformity.

DEPR:

The reason of this effect is not completely clarified yet, although it is supposed as follows. When an abrasive composition without isopropyl alcohol is used, polishing is proceeded in the portion adjacent to a supply port for the abrasive composition, thus lowering polishing uniformity. It is interpreted that, the abrasive grains are charged with electricity because of friction between the polishing pad and the abrasive grains, and the charged grains adsorbed by the polishing pad at its portion adjacent to the supply port for the abrasive composition. It is supposed that, when isopropyl, it controls electrification of the abrasive grains, or charges of the polishing pad and the abrasive grains become of the same sign, thus suppressing adsorption of the grains to the supply port.

DEPR:

In the present invention, the content of isopropyl alcohol is preferably 1 to 15 wt %. When it is 0.5 wt % or less, it has little effect, while when it is 20 wt % or more, uniformity is decreased, probably since the grains are aggregated and the flowability is decreased.

DEPR:

Further, by addition of isopropyl alcohol, the abrasive grains becomes reluctant to adhere to the wafer, thus making cleaning after the polishing easy. Further, a fluid film of isopropyl alcohol is formed on the wafer, and thus, it become easy to dry the wafer in clean conditions due to the so-called Marangoni effect.

DEPR:

Furthermore, it is preferable to deaerate the abrasive composition of the present invention. In some polishing conditions, air may be taken in, or gas may be generated during the polishing process, which becomes cause of decreasing polishing uniformity. By advance deaeration of the gases such as air dissolved in the composition, the composition can dissolve any gas generated during the polishing, thus preventing a decrease of polishing uniformity. As a preferable method of deaeration, a vessel may be divided into two chambers by a membrane, through which only gas is permeable, and then the abrasive composition is made to flow through one chamber and the other chamber is sucked to be vacuum. As the level of the amount of the dissolved gas, one of ppb order is preferable.

DEPR:

The abrasive composition according to the present invention may be used also preferably for polysilicon, aluminum alloy, other metal wiring, or the like embedded in a trench for example, as well as the above-described inter layer insulating film. Further, it can be used not only for polishing a semiconductor surface but also for fine polishing of various materials, of course.

DEPR:

In the present invention, depending on uses, a surfactant may be added by about 100 ppm.

DEPR:

Next, there will be described a method of polishing a semiconductor wafer using the abrasive composition of the present invention.

DEPR:

FIG. 1 shows an example of a polishing apparatus to which the abrasive composition of the present invention is preferably applied.

DEPR:

As shown in FIG. 2, the polishing pad 104 is provided with a plurality of holes 201 for supplying the abrasive composition.

DEPR:

The abrasive composition is supplied through the inside of the rotation axis 103 and the holes 201 into the portion between the wafer 101 and the polishing pad 104.

DEPR:

As shown in FIG. 1, there is employed the polishing pad 104 which is smaller than the wafer 101 for coping with in-plane variation of thickness of the wafer 101. Farther, the apparatus is so arranged that the abrasive composition is presently supplied from the inside of the polishing pad 104, thus the composition being supplied uniformly between the polishing pad 104 and the wafer 101.

DEPR:

The surface of the wafer 101 is polished while the abrasive composition is supplied into the portion between the polishing pad 104 and the wafer 101 with constant pressure, with the polishing pad 104 turning on its axis and revolving, and the wafer 101 being made to turn and swing in the horizontal direction. Preferably, the diameter of the holes made in the polishing pad 104 is 0.5 to 2.5 mm. Uniformity is increased more when a large number of small holes are provided.

DEPR:

The supply rate of the abrasive composition 50 to 100 ml/min. for an 8 inch wafer. Its supplying pressure is about 10 to 100 g/cm.sup.2.

DEPR:

As a material for the polishing pad 104, any material may be used since static electrification can be controlled by using the abrasive composition of the present invention. However, to attain higher uniformity of polishing, it is preferable to use a material having the static electrification of the same sign as the abrasive grains.

DEPR:

Depending on the material or the object to be polished, polishing quantity, and the like, suitable selection may be made on a kind of the abrasive grains, supplying pressure, supply rate, material of the pad, turning speed, revolving speed, swinging, pushing pressure, turning speed of a wafer, and the like.

DEPR:

By using the above-described polishing method, together with high uniformity and polishing speed of the abrasive composition of the present invention, it is possible to perform polishing which requires very high accuracy, such as planarization of a semiconductor surface.

DEPR:

In the present embodiment, to clarify the effect of the abrasive composition of the present invention, polishing is performed in the apparatus shown in FIG. 1 while only the polishing pad 104 is made to turn, without the turning and swinging of the wafer 101 and without the revolving of the polishing pad 104.

DEPR:

As the abrasive composition, there is employed one obtained by dispersing 12 wt % of silica (SiO₂) with grain diameters of 30 to 50 nm into fluid consisting of water and isopropyl alcohol in various

ratios.

DEPR:

The results of polishing are shown in FIGS. 3(b) and 3(a); FIG. 3(b) showing the case of using the composition of the present embodiment added with 5 wt % of isopropyl alcohol, and FIG. 3(a) the case of using the conventional composition without isopropyl alcohol added.

DEPR:

As shown by FIGS. 3(a) and 3(b), it was found that polishing quantities shown by the thickness of the oxide film were large in corresponding to the positions of the holes, which was more obvious in FIG. 3(b) corresponding to the present embodiment. Namely, by adding isopropyl alcohol, uniformity of polishing was increased.

DEPR:

To investigate the reason, charge of electrification was measured using a surface potentiometer for the pad and the abrasive composition just after the polishing. The results are shown in FIG. 4.

DEPR:

As obvious from FIG. 4, in the case of the conventional composition, the pad and the composition are of charges with opposite signs. On the other hand, in the case of the abrasive composition of the present embodiment including isopropyl alcohol, their charges are of the same sign, and the magnitudes are smaller than the conventional case. This fact is interpreted to mean that, in the case of the conventional composition, the abrasive is adsorbed by the pad unevenly, resulting in larger uniformity in polishing, while addition of isopropyl alcohol controls the absorption so that the abrasive grains are supplied all over the contact surfaces of the pad and the wafer to improve polishing uniformity and polishing speed.

DEPR:

Next, in FIG. 5, there are shown average amounts of polishing in the case that polishing is performed for 1 minute using the compositions containing isopropyl alcohol in various ratios.

DEPR:

As obvious from the figure, it is found that polishing speed is increased by adding isopropyl alcohol, and in particular, in the range of 1 to 15 wt %, very high polishing speed can be obtained.

DEPR:

As described above, it is found that by using the abrasive composition of the present invention, high uniformity and high speed of polishing can be obtained.

DEPR:

According to the present invention which provides the abrasive composition comprising abrasive grains, isopropyl alcohol, and water, there can be provided the chemical-mechanical polishing method which can attain very high uniformity and speed in polishing.

DEPU:

201 hole for supplying the abrasive composition

DEPU:

603 abrasive composition Supply pipe

CLPR:

1. An abrasive composition comprising abrasive grains, isopropyl alcohol, and water.

CLPR:

2. The abrasive composition according to claim 1, wherein grain sizes of said abrasive grains are 30 to 250 nm.

CLPR:

3. The abrasive composition according to claim 1 wherein said abrasive grains are SiO₂ sub.2.

CLPR:

4. The abrasive composition according to claim 1 wherein the contents of said abrasive grains and said isopropyl alcohol are 5 to 30 wt % and 1 to 15 wt %, respectively.

CLPR:

5. The abrasive composition according to claim 1 wherein said composition is deaerated.

CCOR:

51/307

CCXR:

252/79.1

CCXR:

51/308

CCXR:

51/309

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Document Number 10

Entry 10 of 43

File: USPT

Apr 27, 1999

DOCUMENT-IDENTIFIER: US 5897375 A

TITLE: Chemical mechanical polishing (CMP) slurry for copper and method of use in integrated circuit manufacture

ABPL:

A method for chemical mechanical polishing (CMP) a copper layer (22) begins by forming the copper layer (22). The copper layer (22) is then exposed to a slurry (24). The slurry (24) contains an oxidizing agent such as H₂O₂, a carboxylate salt such as ammonium citrate, an abrasive slurry such as alumina abrasive, an optional triazole or triazole derivative, and a remaining balance of a solvent such as deionized water. The use of the slurry (24) polishes the copper layer (22) with a high rate of removal whereby pitting and corrosion of the copper layer (22) is reduced and good copper interconnect planarity is achieved. This slurry (24) has good selectivity of copper to oxide, and results in copper devices which have good electrical performance. In addition, disposal of the slurry (24) is not environmentally difficult since the slurry (24) is environmentally sound when compared to other prior art slurries.

about the size

BSPR:

The present invention relates generally to semiconductor manufacturing, and more particularly to, a slurry composition containing hydrogen peroxide, citric acid, ammonium citrate, and alumina abrasive which is used to polish copper interconnects on integrated circuits (ICs).

no surface

BSPR:

However, there is currently no known technology which can effectively plasma etch or wet etch copper materials so that functional copper interconnects are adequately formed over the surface of an integrated circuit. In order to overcome this limitation, copper chemical mechanical polishing (CMP) has been suggested as the most promising alternative which can render proper formation of copper interconnects on an integrated circuit. Therefore, the industry is currently searching for an optimal chemical mechanical polishing (CMP) slurry which can be used to form copper interconnects on an integrated circuit (IC).

BSPR:

It is known in the industry to use one of either H₂O₂ or H₂O₃ as an oxidizing agent in a slurry in order to perform aluminum polishing. It is also known in the art to use one of H₂O₂, KIO₃, Ce(NO₃)₃, Fe(NO₃)₃, and K₂Fe(CN)₆ to polish tungsten material. It is also known to use one of HNO₃, HN₃, OH, or KMnO₄ to perform polishing of copper. Therefore, these chemical compounds have been extensively researched by CMP engineers in an attempt to discover an optimal copper CMP process. However, the use of these known chemicals has not yet produced optimal copper polishing results.

DRPR:

FIGS. 1-5 illustrate, in cross-sectional diagrams, a method for forming a copper interconnect over an integrated circuit (IC) using a chemical

mechanical polishing (CMP) slurry in accordance with the present invention .

DEPR:

Generally, the present invention is a new slurry for use in the integrated circuit (IC) industry in order to form chemically mechanically polished (CMP) copper interconnects. In particular, the slurry taught herein contains an oxidizing agent (e.g., hydrogen peroxide H₂O₂), a citrate salt (e.g., ammonium citrate or potassium citrate), an abrasive slurry (e.g., alumina abrasive or silica abrasive), and a balance of a solvent such as deionized water or an alcohol. In addition, the compound 1, 2, 4-triazole or a triazole derivative such as benzotriazole can be included within the slurry to improve copper polishing planarity.

DEPR:

It has been experimentally shown that the use of this new copper slurry results in an improved removal rate of copper whereby the throughput through a CMP processing tool can be improved. Removal rates of greater than 5000 angstroms per minute have been observed. In addition, experimental results have shown reduced pitting and corrosion of the copper material whereby the speed of the integrated circuit is improved and the yield of the integrated circuit is also improved over prior art copper slurries. In addition, it has been shown that good planarity has been achieved when using the slurry taught herein. Good planarity results in enhanced cross-sectional area of the copper interconnects whereby electrical performance is improved by reducing interconnect resistance. In addition, the selectivity of copper to silicon dioxide when using this slurry is high allowing for polish stopping when performing copper dual inlaid or single inlaid processing. Further, the CMP slurry taught herein is much more environmentally sound than other slurries which are used in the integrated circuit (IC) industry.

DEPR:

After formation of the etch stop layer 18, a dielectric layer 20 is then formed over a top of the etch stop layer 18. The material composition of the layer 20 is similar to the layer 16 which was previously discussed. In addition, the thickness of the layer 20 is comparable to the thickness of layer 16 as previously discussed or is made with layer 16 is up to two times as thick as the layer 20. Known photolithographic processing and convention etch technology is then utilized to form a via opening through the layer 16 and a trench interconnect opening through the layer 20. These openings through the layers 16 and 20 can be formed in a via first manner or a trench first manner as is known in the dual inlaid art. Furthermore, although dual inlaid processing is shown in FIGS. 1-5, the polishing slurry and process taught herein may be used to form single inlaid structures or copper plug regions.

DEPR:

FIG. 2 illustrates that the structure 10 of FIG. 1 is placed into a chemical mechanical processing (CMP) tool. The copper layer 22 of FIG. 1 is placed into contact with a chemical mechanical polishing (CMP) slurry 24 as illustrated in FIG. 2. A chemical mechanical polishing pad 26 is placed in contact with the slurry 24 and is mechanically rotated and applied with pressure in order to result in effective chemical/mechanical removal of upper portions of the layer 22.

DEPR:

FIG. 2 illustrates an oxidized layer 22a which is formed from the layer 22. The layer 22a is an oxidized copper layer which is formed due to the exposure of the layer 22 to the slurry 24 in FIG. 2. In essence, the layer 24 contains an oxidizing species which oxidizes a thin top portion of the layer 22 to form the layer 22a as illustrated in FIG. 2. Other chemical species within the slurry 24 will chemically attack the layer 22a to dissolve layer 22a into the slurry 24. In addition, various particles or abrasive slurry materials within the slurry 24 along with the mechanical movement of the polishing pad 26 results in mechanical abrasion of the layer 22a to further effectuate removal of the layer 22a from the layer 22. Through progressive oxidation and removal of layer

22a and subsequent oxidized Cu layers, top surfaces of the layer 22a are removed to enable effective copper chemical mechanical polishing (CMP).

DEPR:

The slurry 24 illustrated in FIG. 2 contains an oxidizing agent, a carboxylate salt (e.g., a citrate salt), an abrasive slurry, a solvent, and an optional triazole or triazole derivative. Specifically, the oxidizing agent which can be utilized within the slurry is hydrogen peroxide (H₂O₂). Carboxylate salts which have been shown to be effective for removal of copper includes one of many citrate salts such as one or more of ammonium citrate or potassium citrate. A typical abrasive which has been experimentally shown to result in good copper removal and planarization is an alumina abrasive, but a silica abrasive in lieu of the alumina abrasive or in addition with the alumina abrasive may be used. In addition, an optional triazole derivative or triazole solution may be added to the slurry. It was experimentally found, for example, that the addition of 1, 2, 4-triazole to the copper CMP slurry has been shown to improve copper planarization by reducing the amount of copper recessing into oxide trench openings. Typical solvents used in the slurry 24 of FIG. 2 is one or more of deionized water (H₂O) or an alcohol.

DEPR:

In general, the oxidizing agent (H₂O₂) of the slurry 24 may be within any range of roughly 0.2 weight percent (wt %) to 5.0 weight percent (wt %). The carboxylate salt or citrate salt can be within a range of roughly 0.2 weight percent to roughly 20 weight percent. The abrasive slurry (alumina abrasive) is roughly 1.0 weight percent to 12.0 weight percent of the slurry 24. In addition, an optional triazole or triazole derivative can be provided within the slurry 24 to be roughly 0.05 weight percent to 2.0 weight percent of the slurry 24. A remaining balance of the slurry 24 is typically deionized water and/or an alcohol solution.

DEPR:

In a preferred form, it has been experimentally shown that adequate copper (Cu) polishing has been achieved using a hydrogen peroxide range between 1.0 weight and 1.5 weight percent, a citrate salt concentration within the range of 0.8 weight percent and 1.3 weight percent, an alumina abrasive concentration within the range of 2.0 weight percent and 4.0 weight percent, a triazole concentration between roughly 0.1 weight percent and 0.2 weight percent, and a remaining balance solvent. A preferred solution within this range which has been utilized is 1.2 weight percent hydrogen peroxide, 1.1 weight percent ammonium citrate, 3.0 weight percent alumina slurry, 0.12 weight percent, 1, 2, 4-triazole, and a remaining balance deionized water (H₂O).

DEPR:

FIG. 3 illustrates that the previously illustrated layer 22a has been removed by the slurry 24 in conjunction with the mechanical motion of the polishing pad 26. Oxidized layers 22b are continually formed as polishing progresses and as oxidized material is being removed. These oxidized layers 22b, which continually form over time and new Cu atoms are exposed to the slurry, are continually removed by the chemical interaction of the slurry 24 in conjunction with the mechanical interaction of the polishing pad 26. Therefore, as illustrated in FIG. 3, an overall thickness of the layer 22 overlying the dielectric 20 is reduced in thickness while an overall planarity of the layer 22 is gradually improved over time.

DEPR:

FIG. 4 illustrates that chemical-mechanical polishing (CMP) using the slurry 24 continues until a copper interconnect 28 is formed as illustrated in FIG. 4. In a preferred form, the interconnect 28 would be formed co-planar with the top surface of the layer 20. However, some recessing/dishing of the copper layer 22 can occur in most CMP systems resulting in a recessed interconnect 28 as shown in FIG. 4. It is important to note that the presence of the triazole or triazole derivative in the CMP slurry has been experimentally shown to reduce

this adverse recessing of the copper interconnect 28. However, total elimination of the recessing of the layer 28 may not be possible in all applications. FIG. 4 also illustrates that a thin copper oxide layer 22c may be left remaining on a top surface of the interconnect layer 28.

DEPR:

FIG. 5 illustrates that the copper recessing problem illustrated in FIG. 4 can be remedied by performing a subsequent oxide polish in addition to the copper polish illustrated in FIGS. 2-4. In order to perform the oxide polish, a second slurry 30 and a second polishing pad 32 are applied over the top of semiconductor structure 10 in order to perform a second CMP operation. While the polishing pad 32 of FIG. 5 and pad 26 of FIG. 3 may be the same pad on a same CMP tool, the pads 26 and 32 may be different polishing pads on very different CMP tools. The slurries 30 and 24 are preferably different whereby the slurry 30 is optimized for oxide removal selective to copper while the slurry 24 is optimized for copper removal selective to oxide. In FIG. 5, the slurry 30 is typically a silica abrasive which contains KOH and deionized water. This slurry 30 in conjunction with the polishing pad 32 will enable effective removal of a thin top portion of layer 20 whereby the layer 20 is once again made co-planar with the top surface of the copper interconnect 28.

DEPR:

Although the invention has been described and illustrated with reference to specific embodiments, it is not intended that the invention be limited to those illustrative embodiments. Those skilled in the art will recognize that modifications and variations may be made without departing from the spirit and scope of the invention. For example, the thicknesses discussed herein will most likely shrink over time as lithographic feature sizes shrink and technological advancement progresses. Other deposition methods such as low pressure CVD (LPCVD), plasma enhanced CVD (PECVD), physical vapor deposition (PVD), electroless plating, sputtering, and the like may be used to form various layers herein. Other oxidation agents other than H₂O₂ may be used wherein the oxidation agent taught herein can be any chemical that oxidizes copper. Therefore, it is intended that this invention encompass all of the variations and modifications as fall within the scope of the appended claims.

CLPR:

1. A chemical mechanical polishing slurry comprising:

CLPR:

2. The chemical mechanical polishing slurry of claim 1 wherein the solvent is deionized water.

CLPR:

3. The chemical mechanical polishing slurry of claim 1 wherein the solvent is an alcohol.

CLPR:

4. The chemical mechanical polishing slurry of claim 1 wherein the carboxylate salt is a citrate salt.

CLPR:

5. The chemical mechanical polishing slurry of claim 4 wherein citrate salt is ammonium citrate.

CLPR:

6. The chemical mechanical polishing slurry of claim 4 wherein citrate salt is potassium citrate.

CLPR:

7. The chemical mechanical polishing slurry of claim 1 wherein 1,2,4-triazole is added to the chemical mechanical polishing slurry.

CLPR:

8. The chemical mechanical polishing slurry of claim 7 wherein the 1,2,4-triazole is added to the chemical mechanical polishing slurry

within a weight percentage range of 0.05 wt % to 2.0 wt %.

CLPR:

9. The chemical mechanical polishing slurry of claim 1 wherein a triazole derivative is added to the chemical mechanical polishing slurry.

CLPR:

10. The chemical mechanical polishing slurry of claim 9 wherein the triazole derivative is added to the chemical mechanical polishing slurry within a weight percentage range of 0.05 wt % to 2.0 wt %.

CLPR:

11. The chemical mechanical polishing slurry of claim 1 wherein the oxidizing agent is hydrogen peroxide (H₂O₂).

CLPR:

12. The chemical mechanical polishing slurry of claim 1 wherein the abrasive slurry is alumina abrasive.

CLPR:

13. The chemical mechanical polishing slurry of claim 1 comprising:

CLPR:

14. The chemical mechanical polishing slurry of claim 1 comprising:

CLPR:

15. The chemical mechanical polishing slurry of claim 1 wherein the oxidizing agent is hydrogen peroxide, the carboxylate salt is ammonium citrate, and the abrasive slurry is an alumina abrasive.

CLPR:

16. The chemical mechanical polishing slurry of claim 15 wherein a triazole derivative is added to the chemical mechanical polishing slurry.

CLPR:

17. A method for polishing a copper layer on an integrated circuit, the method comprising the steps of:

CLPR:

23. The method of claim 17 wherein the polishing slurry comprises:

CLPR:

24. The method of claim 17 wherein the polishing slurry comprises:

CLPR:

1. 2 wt % of the oxidizing agent;

CLPR:

27. The method of claim 17 wherein the oxidizing agent is hydrogen peroxide.

CLPR:

28. The method of claim 17 wherein the oxidizing agent is hydrogen peroxide, the citrate salt is ammonium citrate, and the abrasive slurry is an aluminum abrasive.

CLPR:

29. The method of claim 28 wherein a triazole derivative is added to the polishing slurry.

CLPR:

30. The method for polishing a copper layer on an integrated circuit, the method comprising the steps of:

CLPR:

32. The method of claim 30 wherein the oxidizing agent is hydrogen peroxide, the citrate salt is ammonium citrate, the abrasive slurry is

an alumina abrasive, and the triazole derivative is 1,2,4-triazole.

CLPV:
0.2 wt % to 5 wt % of an oxidizing agent;

CLPV:
1.0 wt % to 1.5 wt % of an oxidizing agent;

CLPV:
1.2 wt % of an oxidizing agent;

CLPV:
polishing the layer comprising copper with a polishing slurry comprising an oxidizing agent, a citrate salt, an abrasive slurry, and a solvent, wherein a portion of the layer comprising copper overlying the top surface of the dielectric layer is removed and a portion of the layer comprising copper remains and a opening.

CLPV:
performing an oxide polish process after the step of polishing the layer comprising copper.

CLPV:
adding a triazole derivative to the polishing slurry.

CLPV:
adding 1,2,4-triazole to the polishing slurry.

CLPV:
1.0 wt % to 1.5 wt % of the oxidizing agent;

CLPV:
polishing the layer comprising copper with a slurry comprising an oxidizing agent, a citrate salt, an abrasive slurry, a triazole derivative, and a solvent, a portion of the layer comprising copper remains in the via and the interconnect trench while a portion of the layer comprising copper overlying the top surface of the second dielectric layer is removed.

CLPV:
1.0 wt % to 1.5 wt % of the oxidizing agent;

CCXR:
106/3

CCXR:
438/692

CCXR:
51/304

CCXR:
51/306

CCXR:
51/309

ORPL:
J.M. Steigerwald et al., "Mat. Res. Soc. Symp. Proc.," vol. 337, 1994, Method of Chemical Mechanical Polishing Predominantly Copper Containing Metal Layers in Semiconductor Processing, pp. 133-138.

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Document Number 34

Entry 34 of 128

File: USPT

Oct 27, 1998

DOCUMENT-IDENTIFIER: US 5827781 A
TITLE: Planarization slurry including a dispersant and method of using same

ABPL:

A planarization method includes providing a wafer surface and positioning a pad for contact with the wafer surface. The wafer surface is then planarized using the pad and a slurry. The slurry includes a dispersant which is one of any micellar forming surfactants. Preferably, the dispersant is a diprotic acid having 6 or less carbons connecting the acid groups, more preferably a diphosphonic acid with 4 or less carbon atoms connecting the acid groups, and most preferably is 1,2-ethylenediphosphonic acid (EDP). The wafer surface may be either a nonplanar or a substantially planar wafer surface. Another slurry that can be used in the method includes a slurry component including an abrasive component and a chemically interactive component that interacts with the surface. The slurry component when used alone in a planarization of the surface results in a surface thickness uniformity having a first standard deviation and a first rate of removal of material from the surface. The slurry further includes a dispersant component of a quantity sufficient to reduce the first standard deviation to a second standard deviation lower than the first standard deviation when the planarization of the surface is performed with the slurry including the slurry component and the dispersant component. The planarization of the surface performed with the slurry including the slurry component and the dispersant component has a second rate of removal substantially equivalent to the first rate of removal.

BSPR:

Nonionic surfactants have been added to slurries during CMP in an attempt to enhance uniformity of the material removed from the wafer surface. For example, as described in "Uniformity of Removal Rate in the CMP of Silicon Dioxide Films," by K. Achuthan, et al., DIJMIC Conference, Feb. 21-22, 1995, polyethylene oxide (20) stearyl ether (PEO(20)) and polyethylene oxide (10) stearyl ether (PEO(10)) were added to slurries during planarization by CMP. However, the addition of such surfactants reduced the removal rate of the surface material significantly. Reduction of the removal rate is undesirable as it decreases the machine through rate. Further, some surfactants may result in a contaminated surface following cleaning of the surface after CMP is performed.

BSPR:

The planarization method in accordance with the present invention includes providing a wafer surface and positioning a pad for contact with the wafer surface. The wafer surface is then planarized using the pad and a slurry. The slurry includes a dispersant which is one of any micellar forming surfactants. Preferably the dispersant is a diprotic acid having 6 or less carbons connecting the acid groups, more preferably a diphosphonic acid with 4 or less carbon atoms connecting the acid groups, and most preferably is 1,2-ethylenediphosphonic acid (EDP). The wafer surface may be either a nonplanar or a substantially

planar wafer surface.

BSPR:

Another slurry that can be used in the method includes a slurry component including an abrasive component and a chemically interactive component that interacts with the surface. The slurry component when used alone in a planarization of the wafer surface results in a wafer thickness uniformity having a first standard deviation and a first rate of removal of material from the wafer surface. The slurry further includes a dispersant component of an amount sufficient to reduce the first standard deviation to a second standard deviation lower than the first standard deviation when the planarization of the wafer surface is performed with the slurry including the slurry component and the dispersant component. The planarization of the wafer surface performed with the slurry including the slurry component and the dispersant component has a second rate of removal at least substantially equivalent to the first rate of removal.

BSPR:

The slurry of the present invention for use in planarization of a surface of a wafer includes a slurry component including an abrasive component and a chemically interactive component that interacts with the surface of the wafer. The slurry further includes a dispersant component including one of any micellar forming surfactants. Preferably the dispersant is a diprotic acid having 6 or less carbons connecting the acid groups, more preferably a diphosphonic acid with 4 or less carbon atoms connecting the acid groups, and most preferably EDP.

BSPR:

In another embodiment, the slurry includes a slurry component including an abrasive component and a chemically interactive component that interacts with the surface. The slurry component when used alone in a planarization of the surface results in a surface thickness uniformity having a first standard deviation and a first rate of removal of material from the surface. The slurry further includes a dispersant component of a quantity sufficient to reduce the first standard deviation to a second standard deviation lower than the first standard deviation when the planarization of the surface is performed with the slurry including the slurry component and the dispersant component. The planarization of the surface performed with the slurry including the slurry component and the dispersant component has a second rate of removal at least substantially equivalent to the first rate of removal.

DEPR:

The conventional slurry component generally includes an abrasive component and a component that chemically interacts with the surface 12. For example, a typical oxide polishing slurry may consist of a colloidal suspension of oxide particles, with an average size of 30 nm, in an alkali solution having a pH greater than or equal to about 9. Ceria (CeO₂) suspensions may also be used when appropriate, particularly where large amounts of SiO₂ must be removed. Ceria acts as both the chemical and mechanical agent in the slurry. Other abrasive components of the slurry component may include, but are not limited to, alumina (Al₂O₃), silica, titania (TiO₂), or any other abrasive used in conventional planarization slurries as is known to one skilled in the art.

DEPR:

Several slurry solutions presently available include ILD1300, an aqueous colloidal silica slurry including amorphous silica and ammonium hydroxide, available from Rodel, Inc., Newark, Del., and SC-1, a colloidal fumed silica aqueous slurry including amorphous silicon dioxide, DI water, and potassium hydroxide, available from Cabot Corp., Tuscola, Ill., under the trade designation CAB-O-SPERSE SC-1. General characteristics of suitable conventional slurry components utilized in conjunction with the present invention include that the hardness of the polishing particles or abrasive component should be about the same hardness as the hardness of the film being polished to avoid damaging the film. In addition, the particles should be uniform and the solution

should be generally free of metallic contaminants. Further, for example, conventional planarization slurries having a pH greater than about 9 are used for oxide polishing processes and those less than a pH of about 4 are used for polishing processes of, for example, tungsten. The conventional slurry used is dependant upon the type of surface being polished.

DEPR:

A suitable dispersant may include any micellar forming surfactant. In other words, the surfactants must be capable of forming aggregates of molecules or ions referred to as micelles in the slurry of the CMP process. This micelle formation must be capable of being performed in ambient temperature of the CMP process, typically 60.degree. F. to about 140.degree. F., and at the pH of the slurry used, typically either less than about 4 or greater than about 9. The micellar forming surfactant must have limited solubility, i.e. it must not be totally soluble in the CMP slurry or it could not function as a surfactant or a dispersant. Further, the surfactant should have limited buffering affect on the slurry, i.e. it must not be of such a quantity as to affect the slurry pH such that the slurry can no longer function properly as a planarization slurry for the surface being planarized. In order to form micelles, the surfactant must be of a concentration in the slurry that exceeds the critical micelle concentration (CMC). Generally, short chained surfactants have lower CMC values and thus a lesser concentration of the surfactant in the slurry allows the surfactant to function as a dispersant. Such short chain surfactants include short chain organic acids. For example, an oxylate is such a short chain micellar forming surfactant.

CLPR:

3. The method according to claim 2, wherein the slurry includes a first slurry component including an abrasive component and a chemically interactive component that interacts with the wafer surface; and further wherein the EDP is a second slurry component of the slurry in an amount in the range of about 0.001 grams to about 20 grams per 5000 ml of the first slurry component.

CLPV:

planarizing the wafer surface using the pad and a slurry, the slurry including a dispersant, the dispersant being one of any micellar forming surfactants selected from diphosphonic acids with 4 or less carbon atoms connecting the acid groups.

CLPV:

a slurry component including an abrasive component and a chemically interactive component that interacts with the surface of the wafer; and

CLPV:

a dispersant component including one of any micellar forming surfactants selected from diphosphonic acids with 4 or less carbon atoms connecting the acid groups.

CLPV:

a slurry component including an abrasive component and a chemically interactive component that interacts with the surface, the slurry component when used alone in a planarization of the surface resulting in a surface thickness uniformity having a first standard deviation and a first rate of removal of material from the surface; and

CLPV:

a dispersant component which is a micellar forming surfactant selected from diphosphonic acids with 4 or less carbon atoms connecting the acid groups of a quantity sufficient to reduce the first standard deviation to a second standard deviation lower than the first standard deviation when the planarization of the surface is performed with the slurry including the slurry component and the dispersant component, the planarization of the surface performed with the slurry including the slurry component and the dispersant component having a second rate of removal substantially equivalent to the first rate of removal.

CLPV:
a slurry component including an abrasive component and a chemically interactive component that interacts with the surface of the wafer; and

CLPV:
planarizing the oxide layer using the pad and a slurry, the slurry including a dispersant, the dispersant being one of any micellar forming surfactants.

CLPV:
a slurry component including an abrasive component and a chemically interactive component that interacts with the oxide surface layer of the wafer; and

CLPV:
a dispersant component including one of any micellar forming surfactants selected from diphosphonic acids with 4 or less carbon atoms connecting the acid groups.

CLPV:
a slurry component including an abrasive component and a chemically interactive component that interacts with the oxide surface layer, the slurry component when used alone in a planarization of the oxide surface layer resulting in a surface thickness uniformity having a first standard deviation and a first rate of removal of material from the oxide surface layer; and

CLPV:
a dispersant component which is a micellar forming surfactant selected from diphosphonic acids with 4 or less carbon atoms connecting the acid groups of a quantity sufficient to reduce the first standard deviation to a second standard deviation lower than the first standard deviation when the planarization of the oxide surface layer is performed with the slurry including the slurry component and the dispersant component, the planarization of the oxide surface layer performed with the slurry including the slurry component and the dispersant component having a second rate of removal substantially equivalent to the first rate of removal.

CLPW:
~~a slurry component including an abrasive component and a chemically interactive component that interacts with the surface, the slurry component when used alone in a planarization of the wafer surface~~
resulting in a wafer thickness uniformity having a first standard deviation and a first rate of removal of material from the wafer surface; and

CLPW:
a dispersant component which is a micellar forming surfactant selected from diphosphonic acids with 4 or less carbon atoms connecting the acid groups of an amount sufficient to reduce the first standard deviation to a second standard deviation lower than the first standard deviation when the planarization of the wafer surface is performed with the slurry including the slurry component and the dispersant component, the planarization of the wafer surface performed with the slurry including the slurry component and the dispersant component having a second rate of removal substantially equivalent to the first rate of removal.

CCOR:
438/692

CCXR:
438/693

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Document Number 31

Entry 31 of 240

File: USPT

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TITLE: Polishing slurries and a process for the production thereof

ABPL:

5/10/2
A polishing slurry is formed of a silica-dispersed solution obtained by dispersing, in an aqueous solvent, a fumed silica having an average primary particle size of from 5 to 30 nm, the silica-dispersed solution exhibiting a light scattering index (n) of from 3 to 6 at a silica concentration of 1.5% by weight, and the fumed silica dispersed therein having an average secondary particle size of from 30 to 100 nm on the weight basis. The polishing slurry is produced by pulverizing, using a high-pressure homogenizer, a silica-dispersed solution obtained by dispersing a fumed silica in an aqueous solvent, so that the fumed silica possesses an average secondary particle size of from 30 to 100 nm on the weight basis. The polishing slurry is used for polishing semiconductor wafers and inter-layer dielectric in an IC process.

BSPR:

5/10/2
A conventional polishing slurry comprising a silica-dispersed solution can be represented by the one which comprises colloidal silica obtained by using sodium silicate as a starting material. For example, New Ceramics No. 2, pp. 45-46, 1995 discloses a polishing slurry for silicon wafers comprising colloidal silica obtained from sodium silicate. The colloidal silica is synthesized in a liquid phase and is used in the form of a dispersion without being dried, exhibiting small average particle diameter, good dispersion and very good stability in a solution.

BSPR:

Generally, however, the colloidal silica has a low purity and could not be used as a polishing slurry for semiconductor wafers that require high purity or as a polishing slurry for the inter-layer dielectric in the IC process. In particular, the polishing slurry for the inter-layer dielectric causes a serious problem of contamination due to cations such as of heavy metals and, hence, must have a high purity.

BSPR:

To meet these requirements, the above literature proposes a method of obtaining colloidal silica by using an organosilicon compound such as alkoxide as a starting material of colloidal silica.

BSPR:

However, the colloidal silica is produced on an industrial scale maintaining a poor yield. Besides, the method which uses the organosilicon compound involves a problem of an increase in the cost of production due to the starting material.

BSPR:

Moreover, the particles of the colloidal silica are soft and easily adhere strongly on the polished surfaces and cannot be removed to a sufficient degree even by the washing. This means that the polished surfaces are further contaminated when use is made of the colloidal silica containing much impurities, that is obtained by using the sodium

silicate as a starting material.

BSPR:

In addition to the colloidal silica, there has been known a fumed silica which is a fine silica and is obtained on an industrial scale maintaining a good yield by burning a silicon tetrachloride in the hydrogen-oxygen combustion flame. The fumed silica has a primary particle size which is as small as that of the colloidal silica and has a high purity.

Therefore, attempts have been made to use the fumed silica as a polishing slurry to substitute for the polishing slurry which uses the colloidal silica.

BSPR:

The fumed silica having a specific surface area of not larger than 75 $\text{m} \cdot \text{sup.2} / \text{g}$ has an average primary particle size of as relatively large as not smaller than 36 nm as reckoned from the specific surface area that will be described later, and makes it relatively easy to obtain a silica-dispersed solution having good dispersion property. However, the fumed silica that is formed in the flame has hard particles. When the silica-dispersed solution of the fumed silica is used as a polishing slurry, therefore, the polished surfaces tend to be scarred and lose planarity, arousing a problem from the standpoint of using it as a polishing slurry for the semiconductor wafers or for the inter-layer dielectric during the IC process. In the CMP for polishing the inter-layer dielectric (often called wiring layer) as represented by a glass film in the IC process that is drawing attention in recent years, in particular, scars formed on the wiring layer are causing a breakage of the wiring formed thereon. According to the present inventors, furthermore, it has been confirmed that the supernatant liquid forms after the silica-dispersed solution is left to stand for several months; i.e., the silica-dispersed solution has poor preservation stability.

BSPR:

That is, the present invention deals with a polishing slurry comprising a silica-dispersed solution obtained by dispersing, in an aqueous solvent, a fumed silica having an average primary particle size of from 5 to 30 nm, the silica-dispersed solution exhibiting a light scattering index (n) of from 3 to 6 at a silica concentration of 1.5% by weight, and the fumed silica dispersed therein having an average secondary particle size of from 30 to 100 nm on the weight basis.

BSPR:

The invention further deals with a process for producing a polishing slurry by pulverizing, using a high-pressure homogenizer, a silica-dispersed solution obtained by dispersing a fumed silica in an aqueous solvent, so that the fumed silica possesses an average secondary particle size of from 30 to 100 nm on the weight basis.

BSPR:

The light scattering index (n) is found by measuring the spectrum of the silica-dispersed solution by using a commercially available spectrophotometer. First, a reference cell and a sample cell having an optical passage length of 10 mm are filled with the deionized water to calibrate zero point over a wavelength range of from 460 to 700 nm. Next, the silica-dispersed solution is diluted with the deionized water so that the silica concentration of the silica-dispersed solution becomes 1.5% by weight. The sample cell is then filled with the silica-dispersed solution of which the concentration is adjusted to measure the absorbance (τ) over a range of wavelengths (λ) of from 460 to 700 nm. Log (λ) and log (τ) are plotted and, by using the following formula,

BSPR:

To accurately measure the absorbance, it is desired that the range of absorbance is from 0.01 to 3 by taking the sensitivity of the measuring instrument into consideration. For this purpose, therefore, the optical passage length of the cell for measuring the absorbance is set to be 10 mm, and the silica concentration in the silica-dispersed solution which is the polishing slurry is set to be 1.5% by weight, so that the

absorbance can be measured over a range of nearly from 0.01 to 3. As for the range of wavelengths for measuring the absorbance, furthermore, a range of 460 to 700 nm is selected within which a straight line is formed upon plotting $\log(\lambda)$ and $\log(\tau)$, and high sensitivity is obtained. Furthermore, the average secondary particle size is measured by using a centrifugal particle size analyzer. That is, the average secondary particle size is a value found on the weight basis as measured by using the particle size analyzer.

DEPR:

In the present invention, a fumed silica is used for preparing a silica-dispersed solution. The fumed silica can be obtained by a known method of burning a silica tetrachloride in the hydrogen-oxygen combustion flame. Upon changing the preparation conditions, the fumed silica has a specific surface area over a range of from about 50 to about 500 m^2/g . If calculated relying upon the aforementioned formula (1), the silica having specific surface area over a range of 50 to 500 m^2/g has an average primary particle size of from about 55 to about 5 nm .

DEPR:

In the polishing slurry of the present invention, it is necessary that the fumed silica has an average primary particle size of from 5 to 30 nm , preferably, from 5 to 27 nm and, more preferably, from 5 to 23 nm from the standpoint of obtaining good preservation stability and preventing the polished surfaces from being scarred.

DEPR:

That is, when the fumed silica having an average primary particle of larger than 30 nm is used, the obtained silica-dispersed solution exhibits good dispersion property. When left to stand for several months, however, the supernatant liquid becomes clear and precipitate deposits on the bottom of the container, exhibiting poor preservation stability. Besides, the polishing slurry using the fumed silica having such a large average primary particle size raises a problem in that the surfaces being polished tend to be scarred due to a large hardness of the fumed silica.

DEPR:

On the other hand, it is difficult to manufacture the fumed silica having an average primary particle size which is smaller than 5 nm .

DEPR:

As described above, there has been known a polishing slurry obtained by dispersing the fumed silica in an aqueous solvent. The polishing slurry that has been concretely disclosed is using the fumed silica having a specific surface area of not larger than 75 m^2/g (average primary particle size of not smaller than 36 nm) by taking the dispersion property into consideration. Therefore, the polishing slurry using such a fumed silica exhibits poor preservation stability and causes the polished surfaces to be scarred.

DEPR:

In the polishing slurry of the present invention, it is important that the light scattering index (n) is not smaller than 3 and that the average secondary particle size of the fumed silica dispersed in the silica-dispersed solution is from 30 to 100 nm and, particularly, from 30 to 90 nm from the standpoint of suppressing scars on the polished surfaces and obtaining good preservation stability.

DEPR:

As a means for dispersing the fumed silica, the Journal of Ceramic Society of Japan 101(6) pp. 707-712 discloses a silica-dispersed solution treated by ultrasonic waves. However, the silica-dispersed solution treated by ultrasonic waves disclosed in the above literature is the one prepared in a laboratory and exhibits uniform dispersion property and good n value like that of the present invention. However, the secondary aggregated particles of the fumed silica particles are not pulverized to a sufficient degree, from which it is not possible to obtain an average secondary particle size of not larger than 100 nm . Here, the average

secondary particle size found from a particle size distribution curve shown in FIG. 4 of the above literature is about 160 nm which becomes about 130 nm when measured under the same conditions as those of the present invention. The silica-dispersed solution having an average secondary particle size in excess of 100 nm causes the polished surfaces to be scarred and leaves room for improvement from the standpoint of preservation stability.

DEPR:

In the present invention, water or a mixture solvent containing water is used without any limitation as an aqueous solvent that constitutes the polishing slurry. Examples of another solvent used for the mixture solvent may be polar solvents such as alcohols like methanol, ethanol and isopropanol, or ethers or ketones, which may be used in one kind or being mixed together in two or more kinds.

DEPR:

As required, furthermore, a widely known dispersion assistant such as surfactant may be added to the aqueous solvent at a concentration of not larger than 10%, preferably, not larger than 3%, and more preferably, not larger than 1%.

DEPR:

According to the present invention, there is no limitation on the pH of the polishing slurry; i.e., the pH may be suitably determined depending upon the use of polishing. The silica-dispersed solution over a range of from an acidic zone to a weakly alkaline zone has such a problem that it exhibits an increased viscosity. The viscosity of the silica-dispersed solution, however, can be decreased so that it can be easily used by adding thereto a variety of salts such as sodium chloride, potassium chloride, potassium sulfate, potassium carbonate, potassium acetate, ammonium chloride, ammonium sulfate, ammonium carbonate and magnesium sulfate in addition to the surfactant which is the dispersing assistant. The salts may be used in an amount of from 10 ppm to 1% by weight with respect to the silica-dispersed solution.

DEPR:

That is, the polishing slurry obtained by dispersing a fumed silica in an aqueous solvent is pulverized by using a high-pressure homogenizer, so that the fumed silica possesses an average secondary particle size of from 30 to 100 nm on the weight basis.

DEPR:

In the present invention, the pulverization relying upon the high-pressure homogenizer comprises pulverizing the fumed silica by permitting the silica-dispersed solution to continuously pass through an orifice under the application of a high pressure. It is further desired that the pulverization is conducted to such a degree that the average secondary particle size is from 30 to 100 nm and, particularly, from 30 to 90 nm.

DEPR:

As will be understood from the foregoing description, the polishing slurry of the present invention comprises a silica-dispersed solution obtained by dispersing a fumed silica having an average primary particle size of not larger than 30 nm, so as to exhibit a light scattering index (n) of from 3 to 6 at a silica concentration of 1.5% by weight and to assume an average secondary particle size of from 30 to 100 nm on the weight basis. Therefore, the polishing slurry exhibits a high preservation stability, a large polishing rate and excellent polishing characteristics causing the polished surfaces to be scarred little. The polishing slurry can be favorably used for polishing silicon wafers and inter-layer dielectric in the IC process.

DEPR:

Measured by using a spectrophotometer (model Ubest-35 manufactured by Japan Spectroscopic Co., Ltd.). First, a reference cell and a sample cell having an optical passage length of 10 mm were filled with the deionized water to calibrate zero point over a whole range of wavelengths. Next,

the polishing slurry was diluted with the deionized water so that the silica concentration of the silica-dispersed solution became 1.5% by weight. The sample cell was then filled with the diluted solution to measure the absorbance (.tau.) at 241 nm over a range of wavelengths (.lambda.) of from 460 to 700 nm. Log (.lambda.) and log (.tau.) were plotted and, by using the aforementioned formula (2), the inclination (-n) of a line was found based upon the method of least squares. In this case, n was regarded to be a light scattering index.

DEPR:

Into a 5-liter polyethylene container were introduced 2472 g of the deionized water and 168 g of a 1N potassium hydroxide aqueous solution, and were mixed together. Next, 360 g of a fumed silica (REOLOSIL QS-10 manufactured by Tokuyama Co. having a specific surface area of 138 m.sup.2 /g and an average primary particle size of 20 nm reckoned as specific surface area) was thrown into the alkali aqueous solution and was stirred using a rod to effect pre-mixing. The thus obtained silica-dispersed solution exhibited a pH of 10.6, and was subjected to the head-on collision treatment by using a head-on collision jet pulverizer (NANOMIZER LA-31 manufactured by Nanomizer, Inc.) under a pressure of 800 kgf/cm.sup.2 three times to prepare a silica-dispersed solution.

DEPR:

It will be understood from the foregoing Examples that the polishing slurry comprising a silica-dispersed solution having n of not smaller than 3 exhibits excellent preservation stability and polishing rate. It will be further understood that the polishing slurry comprising a silica-dispersed solution having an average secondary particle size of 30 to 100 nm and a degree of mono-dispersion of from 1.2 to 2, makes it possible to obtain excellent planarity of the samples after polishing.

DEPR:

The polishing slurry comprising the silica-dispersed solution obtained by this process exhibited n of 2.77, and in which the silica was dispersed poorly compared to that of Example 1. Therefore, the preservation stability was poorer than that of Examples, and the polishing rate was small. Moreover, the surface roughness of the sample after polishing was 0.33 nm which was inferior to that of Examples.

DEPR:

Into a 5-liter polyethylene container were introduced 2550 g of deionized water and 150 g of piperazine, and were mixed together. Next, 300 g of a fumed silica (REOLOSIL QS-10 manufactured by Tokuyama Co. having a specific surface area of 138 m.sup.2 /g and an average primary particle size of 20 nm reckoned as specific surface area) was thrown into the alkali aqueous solution and was stirred using a rod to effect pre-mixing. The thus obtained silica-dispersed solution exhibited a pH of 11.2, and was subjected to the head-on collision treatment by using a head-on collision jet pulverizer (NANOMIZER LA-31 manufactured by Nanomizer, Inc.) under a pressure of 800 kgf/cm.sup.2 three times to prepare a silica-dispersed solution.

DEPR:

It will be understood from the foregoing Examples that the polishing slurry comprising a silica-dispersed solution having n of not smaller than 3 exhibits excellent preservation stability and polishing rate. It will be further understood that the polishing slurry comprising a silica-dispersed solution having an average particle size of 30 to 100 nm and a degree of mono-dispersion of from 1.2 to 2, makes it possible to obtain excellent planarity of the samples after polishing.

DEPR:

A silica-dispersed solution was obtained by using colloidal silica (SNOWTEX 20L manufactured by Nissan Kagaku Kogyo Co.) obtained from sodium silicate as a starting material, and from which impurity ions were removed as much as possible by ion exchange. The silica-dispersed solution was diluted with pure water so that the silica concentration was 12% by weight, and potassium hydroxide was added little by little so as

to exhibit a pH of 10.3.

DEPR:

The thus obtained silica-dispersed solution exhibited an average primary particle size of 46 nm, an n-value of 3.92, a viscosity of 2.2 mPa.multidot.s, a pH of 10.3, an average secondary particle size of 57 nm, and a degree of mono-dispersion of 1.33. When used as a slurry for the inter-layer dielectric, the silica-dispersed solution exhibited polishing characteristics and preservation stability that were nearly comparable to those of the polishing slurry of the present invention.

DEPR:

Though the n-value was not smaller than 3, the average secondary particle size was not smaller than 100 nm. Therefore, the silica-dispersed solutions exhibited inferior performance such as polishing rate, surface coarseness, preservation stability, etc.

DETL:

TABLE 1

Metal	Specific	Average	Average	element	surface	primary	secondary	Degree
Polishing	Surface	Preserva-	concent-	area	particle	Viscosity	particle	of
mono-	rate	roughness	tion	Ex.	(m/g)	size (nm)	n (mPa .multidot. s)	
pH	size (nm)	dispersion (nm/min)	(nm)	stability (ppm)				

1	138	20	3.15	3.1	10.5	67	1.75	155	0.10	6 months	0.3 or longer	2	138	20
3.06	3.3	10.3	93	1.81	149	0.23	6 months	0.3 or longer	3	138	20	3.29	2.8	
10.3	62	1.52	166	0.09	6 months	0.3 or longer	4	205	13	3.25	3.0	10.5	71	
1.60	142	0.12	12	6 months	1.4 or longer	5	300	9	3.32	3.2	10.1	56	1.56	
0.09	6 months	1.4 or longer	6	380	7	3.39	3.2	10.4	52	1.49	106	0.08	6	
months	1.5 or longer	7	105	26	3.02	2.6	10.3	113	1.91	170	0.25	6 months		
0.3 or longer														

Ex.: Example

DETL:

TABLE 2

Metal	Specific	Average	Average	element	surface	primary	secondary	Degree
Polishing	Surface	Preserva-	concent-	Comp.	area	particle	Viscosity	of
particle	mono-	rate	roughness	tion	Ex.	(m/g)	size (nm)	n (mPa .multidot. s)
pH	size (nm)	dispersion (nm/min)	(nm)	stability (ppm)				

1	138	20	2.77	12.6	10.5	178	2.48	89	0.33	4 months	1.4	2	205	13	2.71	18.6	
10.5	192	2.60	122	0.27	3 months	1.1	3	300	9	2.05	42.7	10.2	202	2.98	*	1	
month	1.5	4	380	7	1.73	*	10.4	216	3.30	*	1 month	1.7	5	105	26	2.90	4.6
10.2	129	1.99	147	0.37	5 months	2.3	6	80	34	2.61	3.2	10.4	141	2.08	126		
0.44	2 months	2.8															

Comp. Ex.: Comparative Example

DETL:

TABLE 3

Metal	Specific	Average	Average	element	surface	primary	secondary	Degree
Polishing	Surface	Preserva-	concent-	area	particle	Viscosity	particle	of
mono-	rate	roughness	tion	Ex.	(m/g)	size (nm)	n (mPa .multidot. s)	pH
pH	size (nm)	dispersion (nm/min)	(nm)	stability (ppm)				

Ex. 8	138	20	3.17	3.1	11.2	80	1.71	455	0.13	6 months	detection or longer					
impossible	Ex. 9	205	13	3.33	3.3	11.2	68	1.66	441	0.10	6 months	detection or longer				
impossible	Ex. 10	380	7	3.60	3.2	11.1	62	1.53	420	0.09	6 months	detection or longer				
impossible	C.E. 7	138	20	2.80	11.8	11.3	151	2.21	386							
C.E. 8	205	13	2.75	17.2	11.2	186	2.56	373	0.32	1 month						
0.41	2 months	1.5	C.E. 9	380	7	1.51	*	11.3	206	2.88	290	0.33	1 month	1.7		

Ex.: Example, C.E.: Comparative Example

DETL:

TABLE 4

	Comp. Ex. 11	Comp. Ex. 12
	Specific surface area (m.sup.2 /g)	
205 380 Ave. primary particle size (nm)	13 7 n 3.07 3.28	Viscosity (mPa
.multidot. s)	3.2 4.3	pH 10.5 10.4 Ave. secondary particle size (nm)
112 Degree of mono-dispersion	1.84 1.96	Polishing rate (nm/min) 132 98
Surface coarseness (nm)	0.22 0.18	Preservation stability 5 months 3
months Metal elements (ppm)	7.9 5.3	

CLPR:

1. A polishing slurry comprising a silica-dispersed solution obtained by dispersing, in an aqueous solvent, a fumed silica having an average primary particle size of from 5 to 30 nm, a light scattering index (n) of the silica-dispersed solution measured at 1.5% by weight of the silica concentration thereof is from 3 to 6, the fumed silica dispersed therein having a weight average secondary particle size of from 30 to 100 nm and the degree of mono-dispersion of the fumed silica in the silica-dispersed solution is from 1.2 to 2.0.

CLPR:

2. A polishing slurry consisting essentially of a silica-dispersed solution obtained by dispersing, in an aqueous solvent, a fumed silica having an average primary particle size of from 5 to 30 nm, wherein the fumed silica dispersed therein has a weight average secondary particle size of from 30 to 100 nm, and the degree of mono-dispersion of the fumed silica in the silica-dispersed solution is from 1.2 to 2.

CLPR:

5. A polishing slurry consisting essentially of a silica-dispersed solution obtained by dispersing, in an aqueous solvent, a fumed silica having an average primary particle size of from 5 to 30 nm, wherein the fumed silica dispersed therein has a weight average secondary particle size of from 30 to 100 nm, the degree of mono-dispersion of the fumed silica in the silica-dispersed solution is from 1.2 to 2, the concentration of fumed silica in the silica-dispersed solution is from 1 to 30% by weight, and the pH of the silica-dispersed solution is from 8 to 13.

CLPR:

6. A method of polishing a material comprising polishing said material with a polishing slurry, wherein the polishing slurry comprises a silica-dispersed solution obtained by dispersing a fumed silica having an average primary particle size of 5 to 30 nm in an aqueous solvent, wherein the fumed silica dispersed therein has a weight average secondary particle size of from 30 to 100 nm, and the degree of mono-dispersion of the fumed silica in the silica-dispersed solution is from 1.2 to 2.

CLPR:

9. A method of polishing a material comprising polishing said material with a polishing slurry, wherein the polishing slurry consists essentially of silica-dispersed solution obtained by dispersing a fumed silica having an average primary particle size of 5 to 30 nm in an aqueous solvent wherein the fumed silica dispersed therein has a weight average secondary particle size of from 30 to 100 nm, and the degree of mono-dispersion of the fumed silica in the silica-dispersed solution is from 1.2 to 2.

CCOR:

134/7

CCXR:

134/1.3

CCXR:

134/2

CCXR:

51/308

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Document Number 10

Entry 10 of 368

File: USPT

Dec 7, 1999

DOCUMENT-IDENTIFIER: US 5997620 A

TITLE: Polishing composition

ABPL:

A polishing composition for polishing a memory hard disk comprising water and at least one abrasive selected from the group consisting of silicon dioxide, aluminum oxide, cerium oxide, zirconium oxide, titanium oxide, silicon nitride and manganese dioxide, which further contains an iron compound dissolved in the composition, said iron compound being selected from the group consisting of iron(III) nitrate, iron(III) sulfate, ammonium iron(III) sulfate, iron(III) perchlorate and an ion salt of an organic acid.

BSPR:

For the above purpose, it used to be common to carry out finishing by one polishing step by means of a polishing composition (hereinafter sometimes referred to as a "slurry" from its nature) comprising aluminum oxide or other various abrasives and water as well as various polishing accelerators. However, by the one polishing step, it has been difficult to satisfy all of the requirements for removing a relatively large waviness as well as surface defects such as nodules and large pits on the substrate surface and for minimizing the surface roughness within a certain period of time. Accordingly, a polishing process comprising two or more steps, has been studied.

*water/oil/oil/colloidal
Surfactant*

BSPR:

For the above purpose, particularly in finishing polishing in two steps, it has been common to carry out polishing by means of a polishing composition prepared in such a manner that aluminum oxide or other abrasive is thoroughly pulverized and adjusted for proper particle size, water is added thereto, and aluminum nitrate or various organic acids and other polishing accelerators are incorporated thereto, or a polishing composition comprising colloidal silica and water. However, the polishing by means of the former polishing composition had a problem that the balance between the mechanical component and the chemical component was poor, and micro protrusions or fine pits tended to form. The polishing by means of the latter polishing composition had a problem such that the stock removal rate was so low that it took a long time for polishing, and the productivity was low, roll off (or "dove off") as an index of sagging of an end face of the substrate tended to deteriorate, or washing after the polishing tended to be difficult.

no oil

BSPR:

The present invention provides a polishing composition for polishing a memory hard disk comprising water and at least one abrasive selected from the group consisting of silicon dioxide, aluminum oxide, cerium oxide, zirconium oxide, titanium oxide, silicon nitride and manganese dioxide, which further contains an iron compound dissolved in the composition, said iron compound being selected from the group consisting of iron(III) nitrate, iron(III) sulfate, ammonium iron(III) sulfate, iron(III) perchlorate and an iron salt of an organic acid.

BSPR:

The abrasive which is suitable for use as the main abrasive among the components of the polishing composition of the present invention, is selected from the group consisting of silicon dioxide, aluminum oxide, cerium oxide, titanium oxide, silicon nitride, zirconium oxide and manganese dioxide. The abrasive is not limited to any particular one of these, but is preferably silicon dioxide. Further, these abrasives may be used in combination as a mixture of a plurality of them.

BSPR:

Silicon dioxide includes colloidal silica, fumed silica and many other types which are different in the methods for their production or in their properties.

BSPR:

For the composition of the present invention, these abrasives may be employed in optional combination as the case requires. When they are used in combination, the manner of the combination, and the proportions of the respective abrasives are not particularly limited.

BSPR:

Among these abrasives, fumed silica, fumed alumina, fumed titania and fumed zirconia have small particle sizes and thus are preferably used as the abrasive for the present invention.

BSPR:

The above abrasive is to polish a surface to be polished by a mechanical action as abrasive grains. Among them, the particle size of silicon dioxide is usually from 0.005 to 0.5 μm , preferably from 0.01 to 0.2 μm , as the average particle size obtained by the surface area measured by a BET method. Likewise, the particle sizes of aluminum oxide, zirconium oxide, titanium oxide, silicon oxide and manganese dioxide are usually from 0.01 to 10 μm , preferably from 0.05 to 3 μm , as the average particle sizes measured by a BET method. Further, the particle size of cerium oxide is usually from 0.01 to 10 μm , preferably from 0.05 to 3 μm , as the average particle size observed by a scanning electron microscope.

BSPR:

If the average particle sizes of these abrasives exceed the above-mentioned ranges, the surface roughness of the polished surface tends to be bad, or scratching is likely to result. On the other hand, if they are less than the above-mentioned ranges, the stock removal rate tends to be very low and impractical.

BSPR:

The content of the abrasive in the polishing composition is usually from 0.1 to 50 wt %, preferably from 1 to 25 wt %, based on the total amount of the composition. If the content of the abrasive is too small, the stock removal rate tends to be low. On the other hand, if it is too much, uniform dispersion tends to be hardly maintained, and the viscosity of the composition tends to be so high that the handling tends to be difficult.

BSPR:

Further, in the composition of the present invention, as the iron compound to be blended, an iron(II) compound may be used so that it may be converted to trivalent in the polishing composition. In such a case, it is preferred that substantially the entire amount of the iron(II) compound be oxidized in the composition to trivalent. This oxidation reaction may be carried out by an addition of an oxidizing agent, or may be carried out by oxygen in air.

BSPR:

The polishing composition of the present invention is prepared usually by mixing and dispersing an abrasive selected from the group consisting of silicon dioxide, aluminum oxide, cerium oxide, zirconium oxide, titanium oxide, silicon nitride and manganese dioxide in water at an optional concentration, and further dissolving the iron compound therein. The

method for dispersing or dissolving these components in water is optional. For example, they may be dispersed by stirring by a vane-type stirring machine or by ultrasonic dispersion. Further, the order of mixing them is optional, and either dispersion of the abrasive or dissolution of the iron compound may be carried out first, or such dispersion and dissolution may simultaneously be carried out.

BSPR:

Further, at the time of preparing the above polishing composition, various known additives may further be added for the purposes of stabilizing or maintaining the quality of the product, or depending upon the type of the object to be treated, the polishing conditions or the necessity for other processing conditions. Preferred examples of such additives include (a) cellulose, carboxymethylcellulose and hydroxyethylcellulose, and other celluloses, (b) ethanol, propanol and ethylene glycol, and other water-soluble alcohols, (c) a sodium alkylbenzenesulfonate and a formalin condensate of naphthalenesulfonic acid, and other surfactants, (d) a lignin sulfonate and a polyacrylate, and other organic polyanionic substances, (e) a polyvinyl alcohol, and other water-soluble polymers (emulsifiers), (f) sodium arginate, potassium hydrogencarbonate, and other bactericides, and (g) soluble metal salts other than the iron compound. Further, it is also possible to employ the above-mentioned abrasive or the polishing accelerator, which is suitable for use in the polishing composition of the present invention, as an auxiliary additive for the purpose other than as the abrasive, for example, for the purpose of preventing settling of the abrasive.

BSPR:

With respect to the reason for the high speed in polishing the Ni--P plating, it is considered that iron ions serve to chemically modify the Ni--P plating surface to make it brittle, and the brittle Ni--P plating surface can readily be removed by the mechanical action of the abrasive. Further, it is considered that the iron ions present in the slurry will contribute to the dispersed state of a certain specific abrasive of the present invention, so that the mechanical polishing speed will be increased by agglomerates having a proper size. It is considered that on other hand, by the iron ions, the agglomeration/dispersion state among the abrasive particles is properly maintained, and formation of excessively large agglomerates is prevented, and at the same time iron ions exhibit a proper level of etching action against the Ni--P plating, whereby the surface roughness tends to be good, and micro protrusions, fine pits and other surface defects will be minimized.

BSPL:

Abrasive

DEPR:

Firstly, as the abrasive, colloidal silica (primary particle size: 0.035 .mu.m), fumed silica, fumed alumina (primary particle size of each: 0.05 .mu.m), fumed zirconia (primary particle size: 0.03 .mu.m), fumed titania (primary particle size: 0.02 .mu.m), aluminum oxide, cerium oxide, silicon nitride and manganese dioxide (primary particle size of each: 0.2 .mu.m) were prepared. These abrasives were respectively dispersed in water by means of a stirrer to obtain slurries having an abrasive concentration of 10 wt %. Then, the iron compounds (in Comparative Examples, the polishing accelerators other than iron) as identified in Table 1 were added and mixed to the slurries, respectively, in an amount of 3 wt %, to obtain test samples of Examples 1 to 16 and Comparative Examples 1 to 6.

DETL:

TABLE 1

Stock removal Surface Micro Fine Abrasive Iron compound rate (.mu.m/min)
roughness (nm) protrusion pits

1 Colloidal Iron(III) 0.13 0.298 .circleincircle. .smallcircle. nitrate 2
Iron(III) .smallcircle.circleincircle. sulfate 3 Ammoniuml

.smallcircle.ircleincircle. iron(III) sulfate 4 Iron(III)
.smallcircle.circleincircle. silica perchlorate 5 Iron(III)
.smallcircle.circleincircle. silica citrate 6 Ammoniuml
.smallcircle.ircleincircle. silica iron(III) citrate 7 Ammoniuin
.smallcircle.circleincircle. iron(III) oxalate 8 Iron(III)
.smallcircle.circleincircle. nitrate 9 Iron(III)
.smallcircle.circleincircle. nitrate 10 Iron(III)
.smallcircle.circleincircle. alumina nitrate 11 Iron(III)
.smallcircle.circleincircle. nitrate 12 Iron(III)
.smallcircle.circleincircle. nitrateia 13 Iron(III)
.smallcircle.ircleincircle. nitrate 14 Iron(III)n
.smallcircle.rcleincircle. nitrate 15 Iron(III)anese
.smallcircle.ircleincircle. dioxide nitrate Comparative 1 Colloidal Nil
.smallcircle.rcleincircle. silica Comparative 2 Fumed Nil
.smallcircle.rcleincircle. silica Comparative 3 Aluminum Aluminum
.smallcircle. oxide nitrate Comparative 4 Aluminum Gluconic acid 0.21
.DELTA. oxide Comparative 5 Fumed Aluminum .smallcircle. nitratealumina
Comparative 6 Fumed Gluconic acid 0.05 .DELTA. alumina

CLPR:

6. The method according to claim 1, wherein a content of the at least one abrasive in the polishing composition is from 0.1 to 50 wt %, based on a weight of the polishing composition.

CLPR:

7. The method according to claim 1, further comprising preparing the polishing composition by mixing the at least one abrasive to form a mixed abrasive, dispersing the mixed abrasive in water and dissolving the iron compound in water.

CLPV:

the polishing composition comprises water and at least one abrasive selected from the group consisting of silicon dioxide, aluminum oxide, cerium oxide, zirconium oxide, titanium oxide, silicon nitride and manganese dioxide, and

CCOR:

106/3

CCXR:

216/89

CCXR:

438/692

CCXR:

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CCXR:

51/307

CCXR:

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CCXR:

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Document Number 1

Entry 1 of 121

File: USPT

Feb 8, 2000

DOCUMENT-IDENTIFIER: US 6022400 A

TITLE: Polishing abrasive grains, polishing agent and polishing method

ABPL:

Surfaces of substrates, typically semiconductor device substrates, are polished with a polishing agent comprising polishing abrasive grains of a metal oxide (e.g. cerium oxide, zirconium oxide or manganese oxide) having a hydrophilic surface and a surface potential (zeta potential) of not more than 50 mV at pH 7 in absolute value, preferably polishing abrasive grains having hydrophilic groups, preferably hydroxyl groups, at the extremities and then cleaned with an aqueous cleaning solution comprising pure water. The polishing abrasive grains remaining on the polished substrate surface can be removed to a satisfactory degree therefrom by simple cleaning using the aqueous cleaning solution only.

BSPR:

The present invention relates to polishing abrasive grains, a polishing agent and a polishing method for use in polishing the surfaces of substrates, particularly semiconductor substrates, so called "bare wafers", and more particularly semiconductor device substrates. The term "semiconductor device substrates" used herein means substrates with a deposited thin film or films including a thin oxide film and a thin metallic film and/or a printed wiring thereon.

BSPR:

According to the conventional polishing method, polishing, typically mirror polishing, of semiconductor device substrate surface is carried out by first supplying a polishing agent onto a polishing cloth-mounted table, and then pressing a substrate mounted on a support plate onto the turning or oscillating table with an appropriate pressing force, thereby polishing and flattening the substrate surface. Then, the polished substrate surface is cleaned to remove grains, particularly polishing abrasive grains of the polishing agent remaining on the substrate surface.

BSPR:

Without the cleaning with a cleaning solution having an adverse corrosive effect on the printed aluminum wirings to avoid the corrosion of wirings, on other hand, another problem such as failure to remove the metallic contamination caused mainly by the remaining polishing abrasive grains from the substrate surface will be involved.

BSPR:

JP-A 2-275629 discloses a polishing method for rinse-polishing a semiconductor device substrate with a diluted solution of an oxidizing agent such as sodium peroxide, sodium chlorate, hydrogen peroxide, ozone, etc. just before the completion of polishing, thereby making the semiconductor device substrate surface hydrophilic.

BSPR:

An object of the present invention is to provide polishing abrasive grains, a polishing agent and a polishing method, capable of removing

polishing abrasive grains remaining on the surface of a polished substrate to a satisfactory degree by simple cleaning using an aqueous cleaning solution comprising pure water after polishing the substrate surface.

BSPR:

In one aspect, the present invention provides polishing abrasive grains.

BSPR:

The present polishing abrasive grains are characterized in that the grains have a hydrophilic surface. Absolute value of surface potential (zeta potential) as an indicator of surface hydrophilic property is in a range of 0 to 50 mV when measured at pH 7.

BSPR:

Method for imparting a surface hydrophilic property to the polishing abrasive grains is not particularly limited, and preferably includes a method for terminating at least a portion, preferably at least 80%, and more preferably the whole of extremities of polishing abrasive grains with hydrophilic functional groups.

BSPR:

The present polishing abrasive grains are preferably composed of oxide of at least one metal species selected from the metal group consisting of light metals, transition metals and rare earth metals, and at least a portion, preferably at least 80%, more and preferably the whole of whose extremities of the polishing abrasive grains has hydrophilic functional groups. The term "light metals" used herein means metals with a small specific gravity such as alkali metals, alkaline earth metals, aluminum, beryllium, magnesium, etc. The term "oxide of metal" used herein means an oxide of preferably aluminum, zirconium, manganese, titanium, cerium, calcium, barium or copper. The term "hydrophilic functional groups" used herein means groups containing such an atom as oxygen, nitrogen, sulfur or the like, including, for example, hydroxyl groups, carboxyl groups, amino groups, carbonyl groups, sulfo groups, etc., and preferably hydroxyl groups.

BSPR:

The present polishing abrasive grains terminated with hydrophilic groups, for example, hydroxyl groups, at the extremities can be prepared by a plasma irradiation method and a sol-gel process (process for preparing an oxide hydrate sol by hydrolyzing a metal alkoxide) known to those skilled in the art using a metal alkoxide containing the relevant metal species as a starting material, among which the sol-gel process is preferable.

BSPR:

Metal alkoxide for use in the sol-gel process is not particularly limited, so long as it is an alcohol ester of a metal species selected from the above-mentioned metal group, but preferably the number of carbon atoms in the alkoxy group is 1 to 4 from the viewpoint of the ease of hydrolysis. Process for preparing a metal alkoxide is not particularly limited, and includes well known processes to those skilled in the art such as processes for reaction of simple metals, metal oxides, metal hydroxides or metal halides with alcohol. A method for terminating the polishing abrasive grains with functional groups such as carboxyl groups, amino groups, carbonyl groups sulfo groups, etc. at the extremities is also not particularly limited, and methods well known to those skilled in the art are available.

BSPR:

The larger the grain size of polishing abrasive grains, the more improved the polishing rate, but the polishing abrasive grains having larger grain sizes than the necessary sizes may damage the substrate. Thus, the grain sizes are usually in a range of 1 to 10,000 nm, preferably 10 to 100 nm, and more preferably 20 to 50 nm.

BSPR:

The present polishing agent comprises the above-mentioned polishing abrasive grains and a solvent. The solvent may contain a dispersion agent such as well known surfactants, etc. or electrolytic ionized water, etc., if required, as well as deionized water. The dispersion agent such as a surfactant, etc. can be contained at a concentration of no more than 10% by weight, preferably no more than 3% by weight, and more preferably 1 to 3% by weight, on the basis of total weight of the solvent. Range of pH of the polishing agent is not particularly limited and can be selected appropriately in view of the desired use. In case of polishing the deposited oxide film of a semiconductor device silicon substrate, pH is 8 to 13, preferably 8 to 12, and more preferably 10 to 12, where pH can be adjusted by adding an amine such as monoethylamine, isopropylamine or the like, KOH, ammonia or the like thereto. In case of polishing the deposited metallic film of the semiconductor device silicon substrate, pH is 2 to 6, preferably 2 to 5, and more preferably 3 to 4, where pH can be adjusted by adding iron nitrate, copper sulfate or the like thereto.

BSPR:

It is preferable that polishing abrasive grains are uniformly dispersed in the polishing agent. For example, the polishing abrasive grains can be brought into a colloidal state or in a uniformly dispersed state by adding a dispersion agent such as a surfactant, etc. thereto, as mentioned above.

BSPR:

The lower the viscosity of a polishing agent, the harder to uniformly disperse the polishing abrasive grains, whereas the higher the viscosity, the harder to polish the semiconductor device silicon substrate while maintaining uniform thickness of the oxide film or metallic film of the semiconductor device silicone substrate. Thus, the viscosity, when measured at 25.degree. C. by the method specified JIS Z 8803 using a rotation viscometer in a dispersion of 1% by weight of polishing abrasive grains in a solvent, is usually 1 to 10 mpa.cndot.s, preferably 1 to 5 mPa.cndot.s, and more preferably 1 to 2 mpa.cndot.s.

BSPR:

The present polishing method comprises a first step of polishing a substrate surface with the above mentioned polishing agent and a second step of cleaning the polished substrate surface from the first step with an aqueous cleaning solution, thereby removing remaining polishing abrasive grains from the polished substrate surface.

BSPR:

Cleaning solution is not particularly limited, so long as it is an aqueous cleaning solution. For example, an aqueous solution comprising ammonia, hydrogen peroxide and pure water usually in a weight ratio of ammonia:hydrogen peroxide:water=1-2:1-5:4-40. The cleaning solution may further contain a chemical such as a chelating agent, e.g. citric acid, in a proportion of 2 to 30% by weight, preferably 2 to 10% by weight, and more preferably 5 to 10% by weight on the basis of total weight of the cleaning solution. Cleaning temperature is not particularly limited and is, for example, in a range of 70.degree. to 90.degree. C.

BSPR:

The present polishing abrasive grains, polishing agent and polishing method are applicable to polishing of semiconductor device substrates, particularly semiconductor device silicon substrates.

BSPR:

The present polishing agent contains polishing abrasive grains having hydrophilic surfaces, particularly those terminated with hydrophilic functional groups at the extremities. Thus, the present polishing agent is very compatible with the aqueous cleaning solution comprising pure water used in the cleaning step following the polishing, and thus can be effectively transferred in to the cleaning solution from the surfaces of polished substrates by simple cleaning thereby facilitating and ensuring removal of the remaining polishing abrasive grains.

BSPR:

For example, when most widely used semiconductor device silicon substrates are to be polished with a polishing agent containing the conventional cerium oxide polishing abrasive grains with no hydrophilic extremities and then cleaned with an aqueous cleaning solution, no electrochemical repulsion force occurs at all between the polished substrates and the polishing abrasive grains remaining on the surfaces of the polished semiconductor device silicon substrates in the cleaning solution due to the material difference between the substrates and the polishing abrasive grains, and thus the polished substrates cannot be cleaned to a satisfactory degree and the polishing abrasive grains still remain even considerably after the cleaning. In the present invention, on the other hand, cerium oxide polishing abrasive grains with hydrophilic extremities are used. That is, the present polishing abrasive grains have a good hydrophilic property as mentioned above, and thus have a good compatibility with an aqueous cleaning solution. Accordingly, the remaining polishing abrasive grains can be readily removed from the polished substrate surfaces with the aqueous cleaning solution and the polished substrate surfaces can be cleaned to a satisfactory degree. Such effects of the present invention can be obtained not only with cerium oxide but also with oxides of metal species selected from the metal group consisting of light metals, transition metals, rare earth metals, etc., so long as they have a hydrophilic surface as mentioned above. According to the present invention, a polishing agent having good polishability and cleaning susceptibility can be obtained with the polishing agent containing a hydrophilic surface, selected from oxides of the above-mentioned metal group.

DRPR:

FIG. 1 shows typical structural formulas in process of forming polishing abrasive grains according to a first embodiment of the present invention.

DRPR:

FIG. 3 shows typical structural formulas in process of forming polishing abrasive grains according to a second embodiment of the present invention.

DRPR:

FIG. 4 shows typical structural formulas in process of forming polishing abrasive grains according to a third embodiment of the present invention.

DEPR:

The present polishing abrasive grains, polishing agent and polishing method will be described in detail below, referring to preferable embodiments, Example and drawings, which are not intended to limit the present invention.

DEPR:

The present invention will be explained below according to a first embodiment, where a semiconductor device silicon substrate is polished with a polishing agent comprising cerium oxide polishing abrasive grains having a hydrophilic surface as metal oxide polishing abrasive grains.

DEPR:

FIG. 1 shows structural formulas in process of forming polishing abrasive grains for the polishing agent according to the first embodiment.

DEPR:

To form the polishing abrasive grains, tetraethoxycerium as a starting material is subjected to a water-addition polycondensation reaction in the presence of a specific catalyst to form a cerium (Ce) network through oxygen atoms and allow the cerium network to grow into a larger network while maintaining the same structure as normal crystal structure of cerium oxide and finally into abrasive grains of cerium oxide. The resulting abrasive grains in this state still contain a large amount of

ethoxy groups and can react with remaining unreacted starting material, resulting in formation of grain size-uncontrollable gel. By subjecting the abrasive grains to distillation at about 100.degree. C. while adding water thereto, the abrasive grains are terminated with hydroxyl groups at the extremities, whereby ultimate polishing abrasive grains having a hydrophilic surface can be obtained. By this treatment, the polishing abrasive grains can be terminated with hydroxyl groups typical of hydrophilic groups at the extremities to such a degree as to make the polishing abrasive grains hydrophilic. Sometimes, "--O--" bonds may be formed by dehydration of adjacent two hydroxyl groups, and such abrasive grains with "--O--" bonds are within the scope of the present invention, if such "--O--" bonds are in such a proportion as not to give any influence on the required hydrophilic property of the abrasive grain surfaces. This will be applicable to second and third embodiments of the present invention which follow. A polishing agent comprising such polishing abrasive grains having a hydrophilic surface can serve to polish substrate surfaces, typically, semiconductor device silicon substrate surfaces.

DEPR:

In the formation of the present polishing abrasive grains, the degree of polymerization (grain size of polishing abrasive grains) can be adjusted by controlling the water-addition polycondensation reaction time. For example, the grain size of the polishing abrasive grains can be adjusted in a range of about 10 to about 10,000 nm.

DEPR:

The present polishing agent used in the polishing step contains cerium oxide polishing abrasive grains having hydroxyl groups typical of the hydrophilic functional groups terminated on the extremities. Thus, the present polish agent has a good compatibility with an aqueous cleaning solution comprising pure water to be used in the cleaning step after the polishing. Accordingly, the cerium oxide polishing abrasive grains remaining on the surfaces of polished semiconductor device silicon substrates can be readily and assuredly removed from the surfaces with the aqueous cleaning solution. A polishing agent comprising cerium oxide polishing abrasive grains with no hydrophilic surface typical of conventional metal oxide polishing abrasive grains cannot be removed to a satisfactory degree from the polished semiconductor device silicon substrate surfaces in the cleaning step, because of material difference between the cerium oxide polishing abrasive grains and the semiconductor device silicon substrates. On the other hand, the present polishing agent having a distinguished hydrophilic property can have good compatibility with and cleaning susceptibility to the aqueous cleaning solution even if cerium oxide is used as a metal oxide for the polishing abrasive grains.

DEPR:

Thus, when the surface of a semiconductor device silicon substrate 1 is polished with a polishing agent according to the first embodiment of the present invention, the polishing abrasive grains remaining on the surface of polished semiconductor device silicon substrate 1 can be removed to a satisfactory degree from the surface by simple cleaning only with an aqueous cleaning solution comprising pure water without any complicated cleaning step as in the conventional cleaning, thereby enabling simple and satisfactory removal of metallic contamination from the surface of polished semiconductor device silicon substrate 1.

DEPR:

A second embodiment of the present invention will be described below, where a polishing agent is used comprising polishing abrasive grains with hydrophilic functional groups terminated on the extremities similar to that of the first embodiment except only that the metal oxide used is different from that of the first embodiment.

DEPR:

FIG. 3 shows structural formulas in process of forming polishing abrasive grains for a polishing agent according to the second embodiment of the present invention, where a zirconium (Zr) network is formed by a

water-addition polycondensation reaction in the presence of a specific catalyst as in the first embodiment, followed by allowing the network to grow into a larger network, while maintaining the same structure as normal crystal structure of zirconium oxide and ultimately into zirconium oxide polishing abrasive grains through a similar treatment to that of the first embodiment. The resulting polishing abrasive grains are terminated with hydroxyl groups typical of hydrophilic groups at the extremities to such a degree as to make the surfaces of the polishing abrasive grains hydrophilic. A polishing agent comprising such polishing abrasive grains can serve to polish substrate surfaces, typically, semiconductor device silicon substrate surfaces.

DEPR:

The polishing agent according to the second embodiment of the present invention contains zirconium oxide polishing abrasive grains having hydroxyl groups typical of the hydrophilic functional groups formed on the extremities. Thus, the present polishing agent has good compatibility with and cleaning susceptibility to an aqueous cleaning solution comprising pure water to be used in the cleaning step after the polishing. Accordingly, the zirconium oxide polishing abrasive grains remaining on the polished semiconductor device silicon substrate surfaces can be readily and assuredly removed from the surfaces with the aqueous cleaning solution. A polishing agent comprising zirconium oxide polishing abrasive grains with no hydrophilized extremities typical of conventional metal oxide polishing abrasive grains cannot be removed to a satisfactory degree from the surfaces of polished semiconductor device silicon substrate surfaces in the cleaning step, because of material difference between the zirconium oxide polishing abrasive grains and the semiconductor device silicon substrates. On the other hand, the present polishing agent having a distinguished hydrophilic property can have good compatibility with and cleaning susceptibility to the aqueous cleaning solution even if zirconium oxide is used as a metal oxide for the polishing abrasive grains.

DEPR:

Thus, when substrate surfaces, typically semiconductor device silicon substrate surfaces, are polished with a polishing agent according to the second embodiment of the present invention, the polishing abrasive grains remaining on the substrate surfaces can be removed to a satisfactory degree from the surfaces by simple cleaning only with an aqueous cleaning solution comprising pure water without any complicated cleaning step as in the conventional cleaning, thereby enabling simple and satisfactory removal of metallic contamination from the polished substrate surfaces.

DEPR:

A third embodiment of the present invention will be described below, where a polishing agent is used comprising polishing abrasive grains with hydrophilic functional groups terminated on the extremities similar to that of the first embodiment except only that the metal oxide used is different from that of the first embodiment.

DEPR:

FIG. 4 shows structural formulas in process of forming polishing abrasive grains for a polishing agent according to the third embodiment of the present invention, where a manganese (Mn) network is formed by water-addition polycondensation reaction in the presence of a specific catalyst as in the first embodiment, followed by allowing the network to grow into a larger network, while maintaining the same structure as normal crystal structure of manganese oxide and ultimately into manganese oxide polishing abrasive grains through a similar treatment to that of the first embodiment. The resulting polishing abrasive grains are terminated with hydroxyl groups typical of hydrophilic groups, at the extremities to such a degree as to make the surfaces of the polishing abrasive grains hydrophilic. A polishing agent comprising such polishing abrasive grains can serve to polish substrate surfaces, typically, semiconductor device silicon substrate surfaces.

DEPR:

The polishing agent according to the third embodiment of the present invention contains manganese oxide polishing abrasive grains having hydroxyl groups typical of the hydrophilic functional groups terminated at the extremities. Thus, the present polishing agent has good compatibility with and cleaning susceptibility to an aqueous cleaning solution comprising pure water to be used in the cleaning step after the polishing. Accordingly, the manganese oxide polishing abrasive grains remaining on the polished substrate surfaces can be readily and assuredly removed from the surfaces with the aqueous cleaning solution. A polishing agent comprising manganese oxide polishing abrasive grains with no hydrophilic extremities typical of conventional metal oxide polishing abrasive grains cannot be removed to a satisfactory degree from the polished substrate surfaces in the cleaning step because of material difference between the manganese oxide polishing abrasive grains and the semiconductor device silicon substrates. On the other hand, the present polishing agent having a distinguished hydrophilic property can have good compatibility with and cleaning susceptibility to the aqueous cleaning solution even if manganese oxide is used as a metal oxide for the polishing abrasive grains.

DEPR:

Thus, when substrate surfaces, typically semiconductor device silicon substrate surfaces, are polished with a polishing agent according to the third embodiment of the present invention, the polishing abrasive grains remaining on the polished substrate surfaces can be removed to a satisfactory degree from the surface by simple cleaning only with an aqueous cleaning solution comprising pure water without any complicated cleaning step as in the conventional cleaning, thereby enabling simple and satisfactory removal of metallic contamination from the polished substrate surfaces.

DEPR:

The foregoing first to third embodiments of the present invention show cerium oxide, zirconium oxide and manganese oxide as metal oxide with hydrophilic functional groups terminated at the extremities, but the present invention is not limited to only these three species. Besides the above-mentioned metal oxides, other oxides of transition metals and rare earth metals and oxides of light metals such as aluminum oxide, etc. can be used as polishing abrasive grains in the present invention.

DEPR:

Semiconductor device silicon substrate surfaces were polished with the present polishing agent comprising polishing abrasive grains with hydrophilic surfaces and then cleaned in dip-type, cleaning equipment as shown in the foregoing first embodiment of the present invention. The degree of cleaning of polished semiconductor device silicon substrate surfaces was examined in comparison with those obtained with the conventional polishing agent. The values of the surface potential (the zeta potential) of the polishing abrasive grains of the examples are shown in the following. These values are indication which show as to whether or not the grains in a solution liable to attach to the substrate surfaces.

DEPR:

That is, polishing agents Nos. 1 to 4 were prepared by mixing silicon oxide grains (surface potential (zeta potential) at pH 7:-23 mV), cerium oxide grains (surface potential (zeta potential) at pH 7:-35 mV), zirconium oxide grains (surface potential (zeta potential) at pH 7:-42 mV) or manganese oxide grains (surface potential (zeta potential) at pH 7:-28 mV), each of which was terminated with hydroxyl groups at the extremities and had an average grain size of about 500 nm, with a surfactant and pure water, followed by pH adjustment to 10 by addition of KOH thereto. The surface potential of grains measured using a zeta potential meter, Coulter Delsa 440, trademark of products made by Coulter Corporation, (U.S.A.) by the method specified in the catalogue. The polishing agent each had a metal oxide content of 1% by weight and a viscosity of about 1 mpa.cndot.s followed by the method specified JIS Z 8803 using a rotation viscometer as measured at 25.degree. C. For controls, conventional polishing agents Nos. 5 to 8 of Table 1 were

used, each of the grains had no hydrophobic groups at the extremities.

DEPR:

Surfaces of semiconductor device silicon substrates (8 inches (200 mm) in diameter) were polished with the above-mentioned polishing agents, respectively, at a polishing temperature of 25. degree. C., with a table turning rate of 30 r/min and a pressing force of 4 psi (27579 Pa). Polishing rates of an oxide film deposited on the substrates were found to be about 150 nm/min for the polishing agents Nos. 1 and 5 each containing silicon oxide polishing abrasive grains, about 300 nm/min for the polishing agents Nos. 2 and 6 each containing cerium oxide polishing abrasive grains, about 250 nm/min for the polishing agents Nos. 3 and 7 each containing zirconium oxide polishing abrasive grains and about 300 nm/min for the polishing agents Nos. 4 and 8 each containing manganese oxide polishing abrasive grains, and it was found that the polishing rate had no substantial influence by the presence or absence of hydrophilic groups at the extremities.

DEPR:

Then, the polished semiconductor device silicon substrate surfaces were cleaned with an aqueous cleaning solution at 70. degree. C. in dip-type cleaning equipment shown in FIG. 2(c), and then grains having diameters of at least 0.2 .mu.m remaining on the cleaned substrate surfaces were counted. The aqueous cleaning solution used was a solution comprising ammonia; hydrogen peroxide and pure water in a ratio of 1:2:20 by weight.

DEPR:

As is obvious from the results of cleaning in the case of using the conventional polishing agents each comprising metal oxide polishing abrasive grains having diameters of at least 0.2 .mu.m, as shown in Table 1, number of polishing abrasive grains remaining on the cleaned substrate surfaces was in the order of 100, for silicon oxide grains (No. 5), and in the order as large as 1,000 for cerium oxide grains (No. 6), zirconium oxide grains (No. 7), and manganese oxide grains (No. 8), whereas in case of using the present polishing agents the number of cerium oxide grains (No. 2), zirconium oxide grains (No. 3) and manganese oxide grains (No. 4) remaining on the cleaned substrate surfaces could be reduced to the order of 10 equivalent to that of the remaining silicon oxide grains (No. 1).

DEPR:

Thus, the number of polishing abrasive grains remaining on the surfaces of polished substrates could be remarkably reduced on the order of 10 by simple cleaning in case of using the present polishing agents.

DEPR:

Thus, as polishing abrasive grains silicon oxide grains having a surface potential (zeta potential) of not more than 25 mV, cerium oxide grains having a surface potential of not more than 40 mV, zirconium oxide grains having a surface potential of not more than 45 mV and manganese oxide grains having a surface potential of not more than 30 mV at pH 7 in absolute values are preferably used.

DEPR:

In the foregoing test, cleaning of polished substrate surfaces was carried out in dip-type cleaning equipment. To ensure the cleaning, fine grains remaining on the surfaces of polished substrates may be removed by mechanical cleaning using a brush. For example, as shown in FIGS. 5(a) and 5(b), a semiconductor device silicon substrate 1 is transferred to a support plate 3 from a substrate carrier 2 and polished to flatten the surface of the semiconductor device silicon substrate 1 in the same manner as in FIG. 2. Then, as shown in FIG. 5(c), the polished semiconductor device silicon substrate 1 is passed through between a pair of brushes 11 to clean the surface of the polished semiconductor device silicon substrate 1, whereby the number of polishing abrasive grains remaining on the surface of semiconductor device silicon substrate 1 can be reduced to about 10, and the polishing abrasive grains retained in the brushes can be also removed therefrom by

continuous rinsing of the brushes, because the polishing abrasive grains have a hydrophilic property. That is, contamination of successive semiconductor device silicon substrates by the polishing abrasive grains released from the substrate surface and retained in the brushes can be prevented.

DEPR:

According to the present invention, polishing abrasive grains remaining on the polished substrate surfaces can be removed to a satisfactory degree by simple cleaning only with an aqueous cleaning solution comprising pure water etc. without any conventional complicated cleaning, after polishing of the substrate surfaces, whereby metallic contamination can be simply removed to a satisfactory degree from the polished substrate surfaces.

CLPR:

3. A method for polishing a substrate surface with a polishing agent comprising polishing abrasive grains and a solvent, the method comprising:

CLPR:

4. A method for polishing a substrate surface with a polishing agent comprising polishing abrasive grains and a solvent, the method comprising:

CLPV:

polishing abrasive grains having a hydrophilic surface and a surface potential (zeta potential) with an absolute value of not more than 50 mV at pH 7, the polishing abrasive grains being selected from the group consisting of cerium oxide grains having a surface potential with an absolute value of not more than 40 mV at pH 7 and manganese oxide grains having a surface potential with an absolute value of not more than 30 mV at pH 7.

CLPV:

polishing abrasive grains having hydrophilic functional groups at least at a portion of their extremities, the polishing abrasive grains being composed of an oxide of at least one metal species selected from the group consisting of, barium and copper.

CLPV:

polishing a substrate surface with polishing abrasive grains having a hydrophilic surface and a surface potential (zeta potential) with an absolute value of not more than 50 mV at pH 7, the polishing abrasive grains being selected from the group consisting of cerium oxide grains having a surface potential with an absolute value of not more than 40 mV at pH 7 and manganese oxide grains having a surface potential with an absolute value of not more than 30 mV at pH 7.

CLPV:

polishing a substrate surface with polishing abrasive grains having a hydrophilic surface and a surface potential (zeta potential) with an absolute value of not more than 50 mv at pH 7, the polishing abrasive grains being composed of oxide of at least one metal species selected from the metal group consisting of manganese, barium and copper.

CCOR:

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CCXR:

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CCXR:

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CCXR:

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Document Number 120

Entry 120 of 128

File: USPT

May 13, 1986

DOCUMENT-IDENTIFIER: US 4588421 A

TITLE: Aqueous silica compositions for polishing silicon wafers

ABPL:

A composition useful in polishing silicon wafers and like materials which comprises an aqueous colloidal silica sol or gel and from 0.1-5% by weight based on the SiO₂ content of the sol or gel of piperazine.

BSPR:

U.S. Pat. No. 3,170,273, the disclosure of which is incorporated herein by reference, shows that colloidal silica and silica gels are useful as polishing agents for the surfaces of semi-conductor crystals which are most often used in the manufacture of semi-conductor devices. The siliceous polishing agents of this patent are particularly suited to producing highly polished surfaces on silicon crystal wafers, thus rendering these surfaces suitable for the disposition of an epitaxially deposited crystal layer.

BSPR:

The colloidal silica as a sol and silicate gels used by the patentee have an ultimate particle size of 4-200 nanometers. From a commercial standpoint, it is preferred to use as the polishing agents in the process of the patent aqueous colloidal silica sols having particle sizes within the range of 4-100 nanometers.

BSPR:

A substantial improvement in polishing efficiency over U.S. Pat. No. 3,170,273 is disclosed in U.S. Pat. No. 4,169,337. The disclosure is incorporated herein by reference. In accordance with that invention, it was found that semi-conductor surfaces of the type previously described and, most particularly, silicon, can be efficiently polished by using as the polishing agent a combination of either a colloidal form of silica or silica gel having an ultimate particle size within the range of 4-200 nanometers and, preferably, 4-100 nanometers, with a water-soluble amine. The amount of amine in relation to the silica present in the silica sol or gel may range between 0.5-5.0% based on the SiO₂ content of the sol or gel. The preferred amount of the amine is 1.0-5.0% and, most preferably, it is 2.0-4.0%.

BSPR:

Typical water-soluble quaternary ammonium salts and bases that can be used in the invention of U.S. Pat. No. 4,462,188 are tetramethyl ammonium chloride, tetramethyl ammonium hydroxide, dimethyl diethyl ammonium chloride, N,N dimethyl morpholinium sulfate and tetrabutyl ammonium bromide. Of these materials, tetramethyl ammonium chloride is preferred.

BSPR:

The invention comprises an improved method for polishing silicon wafers and like materials which comprises using as a polishing agent a colloidal silica or a gel which is combined with 0.1%-5% by weight of a

piperazine or a lower alkyl nitrogen-substituted piperazine based on the SiO₂ content of the sol. The piperazine may be combined with an additional 0.1-5% by weight of a water-soluble quaternary ammonium salt or base which contains not more than 6 carbon atoms.

BSPR:

As indicated, a wide variety of aqueous colloidal silicas or gels may be used in the practice of the invention. The colloidal silicas are preferred. Two such materials are sold under the designation NALCOAG 1050 and NALCOAG 1060. These silica sols and their properties are described below:

BSPV:

1. Piperazine at a 2% level requires less colloidal silica than aminoethylethanolamine to give the same polishing rate.

BSPV:

2. Piperazine in the presence of colloidal silica shows no discoloration of the product with time.

BSPV:

3. Piperazine at a 2% level in the presence of colloidal silica requires no additional chemical to kill or inhibit microbiological growths.

BSPV:

5. Fumed silica aqueous/dispersions in the presence of piperazine show +10.6% to +18.2% improvement in polishing rate over colloidal silicas containing piperazine at the same silica level (2.4%) or with colloidal silicas containing aminoethylethanolamine at a higher silica level (3.2%). For example, 30 grams of Cabosil M-5 were dispersed in 67.78 grams of water containing 0.22% potassium hydroxide and 2.0% piperazine flake. The dispersed fumed silica formulation, when diluted one part product plus fourteen parts of water, produced the above polishing results.

BSTL:

NALCOAG 1050 Colloidal silica as
 SiO₂ = 50% pH = 9.0 Average Particle Size = 16-25 nm Average
 Surface Area = 120-176 M²/gram Specific Gravity (at 68. degree. F.) = 1.390 Viscosity = 70 cps (maximum) Na₂O content = 0.4% NALCOAG 1060 Colloidal silica as SiO₂ = 50% pH = 8.5 Average Particle Size = 50-70 nm Average Surface Area = 40-60 M²/gram Specific Gravity (at 68. degree. F.) = 1.390 Viscosity at 77. degree. F. = 15 cps (maximum)

DEPR:

In the tests to be described hereinafter, the compositions of the invention were compared against a commercial silica gel amine-containing product which is of the type described in U.S. Pat. No. 4,169,337. This product is an aqueous colloidal silica gel. It has an average particle size of 50-100 nanometers, is sodium stabilized, and contains 50% by weight of colloidal silica particles and 2% by weight of aminoethylethanolamine. Similar results are obtained with piperazine plus bases other than sodium hydroxide. This commercial material is hereafter referred to as Composition 1.

DEPR:

In all of the compositions listed above, unless otherwise mentioned, the starting silica material was colloidal silica used in Comp. 1 diluted to 40% by weight silica. Also, in all of the tests listed, piperazine was used.

DETL:

TABLE VI		EFFECT OF PARTICLE SIZE		
AND PIPERAZINE CONCENTRATION ON POLISHING RATE		% Change Silica Sol PD	Piperazine (1)	Polishing Rate* from Used (nm)
		Concentration (mils/10 min.)		Nalco 1050 20 5%
Comp. 1				
1.42	+1.4%	Nalco 1060 60 5%	1.43 +2.1%	Exp..sub.Sol Silica 75 2% 1.46
+4.3%	Exp..sub.Sol Silica 75 4%	1.47 +5.0%	Exp..sub.Sol Silica 75 5%	

1.59 +13.6% Exp..sub.Sol Silica 75 7% 1.41 +0.7% Exp..sub.Sol Silica 75
10% 1.27 -9.3% Comp. 1 Polishing
Rate = 1.40 mils/10 min.

CLPR:

1. An improved method for polishing silicon wafers and like materials which comprises polishing them with a polishing agent comprising an aqueous colloidal silica sol or a gel which is combined with 0.1%-5% by weight of a piperazine or a lower alkyl nitrogen-substituted piperazine based on the SiO._{sub.2} content of the sol.

CLPR:

2. An improved method for polishing silicon wafers and like materials which comprises polishing them with a polishing agent comprising an aqueous colloidal silica sol or a gel which is combined with 0.1%-5% by weight of piperazine based on the SiO._{sub.2} content of the sol.

CLPR:

3. An improved method for polishing silicon wafers and like materials which comprises polishing them with a polishing agent comprising an aqueous colloidal silica sol or a gel which is combined with 0.1%-5% by weight of a lower alkyl nitrogen-substituted piperazine based on the SiO._{sub.2} content of the sol.

CLPR:

4. An improved method for polishing silicon wafers and like materials which comprises polishing them with a polishing agent which comprises an aqueous colloidal silica sol or a gel which is combined with 0.1%-5% by weight of a piperazine or a lower alkyl nitrogen-substituted piperazine based on the SiO._{sub.2} content of the sol and from 0.1-5% by weight of a water-soluble quaternary ammonium salt or base which contains not more than 6 carbon atoms.

CLPR:

5. An improved method for polishing silicon wafers and like materials which comprises polishing them with a polishing agent which comprises an aqueous colloidal silica sol or a gel which is combined with 0.1%-5% by weight of piperazine based on the SiO._{sub.2} content of the sol and from 0.1-5% by weight of a water-soluble quaternary ammonium salt or base which contains not more than 6 carbon atoms.

CLPR:

6. An improved method for polishing silicon wafers and like materials which comprises polishing them with a polishing agent which comprises an aqueous colloidal silica sol or a gel which is combined with 0.1%-5% by weight of a lower alkyl nitrogen-substituted piperazine based on the SiO._{sub.2} content of the sol and from 0.1-5% by weight of a water-soluble quaternary ammonium salt or base which contains not more than 6 carbon atoms.

CLPR:

7. A composition useful in polishing silicon wafers and like materials which comprises an aqueous colloidal silica sol or gel and from 0.1-5% by weight based on the SiO._{sub.2} content of the sol or gel of piperazine.

CLPR:

8. A composition useful in polishing silicon wafers and like materials which comprises an aqueous colloidal dispersion of fumed silica having a primary particle size within the range 5-200 nanometer and which additionally contains from 0.1 to 5.0% by weight, based on fumed silica content, of piperazine or a lower alkyl nitrogen-substituted piperazine.

CCOR:

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Document Number 35

Entry 35 of 43

File: USPT

Sep 6, 1988

DOCUMENT-IDENTIFIER: US 4769073 A

TITLE: Ceric oxide/cerous salt organic glass polishing compositions

ABPL:

Cerium-based polishing compositions, well adapted for the rapid and efficient polishing of organic glass surfaces, e.g., plastic ophthalmic lenses and plastic sheet material, are comprised of intimate admixture of particulate ceric oxide and a water soluble cerous salt.

BSPR:

The present invention relates to cerium-based polishing compositions especially adapted for the polishing of organic glasses, and, more particularly, for the polishing of plastic ophthalmic lenses and plastic sheet material.

BSPR:

By the term "organic glasses" are intended all organic shaped articles requiring polishing for any given end application. These include, for example, synthetic polymers, most typically polycarbonates, in particular polydiallylglycol carbonates in the form of ophthalmic lenses or in the form of sheet material, e.g., automotive windows and windshields.

BSPR:

The polishing of organic glasses is quite delicate and difficulties therein focus on the fact that they are soft, fragile and very sensitive to scratching. Inadequate polishing results in fine scratches and polishing that is too abrasive may result in coarse scratches, streaks, or even a haze.

BSPR:

While the polishing composition must make it possible to impart a good surface condition onto the organic glass substrate, it must be borne in mind that economic requirements mandate a polishing efficiency sufficient to keep pace with the rate of industrial production.

BSPR:

Polishing compositions usually consist of an abrasive powder in suspension in an organic or aqueous medium, optionally containing other additives.

BSPR:

Exemplary of such abrasive materials, alumina, tin oxide, or mixtures thereof, are currently widely used. If these oxides are contained in the polishing composition, the polishing efficiency is good, but the quality of the polished finish of the organic glass is mediocre in light of deteriorating transparency caused by the presence of a haze and poor surface conditions due to scratching.

BSPR:

It has been suggested in this art to improve these results by using an oxide of a rare earth, in particular ceric oxide. The polishing of

organic glasses using an aqueous suspension of ceric oxide has not to date been satisfactory, as numerous fine scratches remain on the surface of the organic glass due to insufficient polishing.

BSPR:

To obviate the aforementioned disadvantages, in German Pat. No. 2,508,871 a polishing compound having the following composition by weight has been proposed: 30% to 45% cerium oxide having a grain size less than 36 .mu.m, 5% to 15% glycerin and 45% to 60% water.

BSPR:

However, the polishing times required in the use of such composition are longer than those required for polishing with the conventional oxides.

BSPR:

Furthermore, the final polish is not entirely satisfactory, if it is desired to perform certain surface treatments, such as anti-reflection or anti-abrasion treatments, on ophthalmic lenses, which require an excellent quality of the support, as they accentuate the presence of any defect.

BSPR:

To improve the quality of the polish and to reduce the polishing time by 10% relative to that required when using ceric oxide alone, French Pat. No. 2,414,071 describes a polishing material containing ceric oxide in suspension in water and combined with a thickener, such as carboxyethylcellulose, ethylcellulose, methylcellulose, polyvinyl alcohol, sodium polyacrylate, polymethylene oxide, carboxypolymethylene, polyvinylpyrrolidone, casein, gum arabic, and a surface tension reducing agent such as an alkaline alkylaryl sulfonate, lauryl sulfonate, dodecyl sulfonate, dodecyl sulfate, lauryl ether sulfate, dioctyl sulfosuccinate, dihexyl sulfosuccinate, diamyl sulfosuccinate, phosphoric acid polyesters and polysiloxanes.

BSPR:

The surface finish obtained by using the aforementioned composition is satisfactory. However, it remains necessary to further improve the polishing time, as an increase of 10% is still inadequate in view of the present rates of industrial production of ophthalmic lenses.

BSPR:

Accordingly, a major object of the present invention is the provision of an improved polishing agent for the organic glasses, one that not only imparts a high quality surface finish, but which is also highly efficient and permits polishing times comparable to those associated with the conventional oxides of the prior art.

BSPR:

Briefly, the present invention features an improved polishing composition comprising ceric oxide and a water-soluble cerous salt which remains soluble under the conditions of polishing.

BSPR:

It is in powder form having particle dimensions less than approximately 20 .mu.m. Preferably, a ceric oxide having dimensions ranging from 0.1 .mu.m to 10 .mu.m is used; the grain size analysis being carried out using a Sedigraphic 5000 D instrument, which measures the rate of sedimentation of the particles in suspension and automatically displays the results in a cumulative percentage distribution as a function of equivalent spherical diameters (based on Stoke's law).

BSPR:

Preferably, a polishing agent containing at least approximately 30% by weight of ceric oxide is used.

BSPR:

The cerium is preferably introduced into the reaction medium in the cerous state and is then oxidized to the ceric state by continuously adding to the reaction mixture, in a solution other than that containing

the base, an oxidizing agent compatible with said medium. Exemplary of the oxidizing agents suitable for use herein, the following are particularly representative: solutions of sodium, potassium or ammonium perchlorate, hypochlorite or persulfate, hydrogen peroxide, or air, oxygen or ozone. It is also possible to oxidize the cerium electrochemically. Preferably, hydrogen peroxide is used.

BSPR:

The compositions produced according to the procedure described above may be optionally subjected to the operations of grinding and grain size selection utilizing techniques well known to this art.

BSPR:

The mixture of the different solutions of the aforementioned reagents may be carried out according to any one of a number of different techniques. For example, the admixture may be effected under agitation by continuously and separately adding the cerium salt, optionally the solution of the oxidizing agent, the solution of the rare earth salt or salts, the solution of the oxygen derivative or derivatives of silicon and the basic solution. It is also possible to prepare a premixture of the cerium salt solution and the solution of the rare earth salt or salts, which premixture is then added continuously to the reaction medium in parallel with the two other solutions. A premixture of the solution of the oxygen derivative or derivatives of silicon and the basic solution may also be formulated. If an oxidizing agent is used, it is possible to use it in admixture with a solution other than the basic solution, in particular in admixture with the cerium salt solution and/or the solution of the rare earth salt or salts.

BSPR:

The calcined material is then ground such that it will have aggregate dimensions of from 0.2 to 5.0 .mu.m. Typically, the size of the aggregates expressed as the mean diameter ranges from 0.5 to 1.5 .mu.m. The mean diameter is defined as a diameter such that 50% by weight of the aggregates have a diameter larger or smaller than the mean diameter.

BSPR:

The grinding operation may be accompanied by a grain size selection process which may be carried out simultaneously or successively.

BSPR:

The proportions of the ceric oxide and the rare earth oxides in the polishing composition described in French patent No. 2,545,830 may be within the following limits:

BSPR:

It is possible to prepare the mixture of the different solutions of the aforementioned reagents according to any one of a number of different variants. For example, the admixture may be carried out under agitation by continuously and separately adding the solution of the cerium salt, optionally the solution of the oxidizing agents, the solution of the salt or salts of the rare earth or earths and the basic solution. It is also envisaged to effect a premixture of the solution of the cerium salt and the solution of the salt or salts of the rare earth or earths, which is added continuously to the reaction medium in parallel with the basic solution. If an oxidizing agent is employed, it is possible to use it in admixture with the solution of the cerium salt and/or the solution of the salt or salts of the rare earth or earths.

BSPR:

The calcined product is ground and, optionally, a grain size selection operation is carried out, as in French patent No. 2,549,846.

BSPR:

Consistent herewith, in the subject polishing compositions for the polishing of organic glasses, either ceric oxide alone or in the form of a compound thereof, and a cerous salt, are present.

BSPR:

Respecting the cerous salt, any salt of cerium (III) that is soluble under the conditions of polishing is suitable. This cerium (III) salt must be soluble in water, or water slightly acidified to a pH lower than 7.

BSPR:

The polishing compositions according to the invention may be in the form of an aqueous suspension, the concentration in ceric oxide of which may vary over wide limits, for example, from 50 to 600 g/l, but it preferably ranges from 250 to 450 g/l.

BSPR:

The compositions of the invention, whether in the form of an aqueous suspension or a powder, are useful for the polishing of all organic glasses.

BSPR:

Thus, they may be used to polish organic glasses produced from thermoplastic polymers, such as cellulose, cellulose diacetate, reinforced aceto-butyrate, polymethylmethacrylate and polystyrene, or monoplastic polymers, such as plasticized urea-formaldehyde, polydiallylphthalate, polydiallylglycol carbonate, etc.

BSPR:

The subject compositions are especially suitable for the polishing of organic glasses of polydiallyldiethylene glycol carbonate.

BSPR:

The field of application of the invention is not limited to the polishing of ophthalmic lenses, and includes the polishing of all organic glasses, regardless of the form in which they exist.

BSPR:

The compositions of the invention are used for the polishing of glass in conventional manner. As they are typically employed in a spray polishing system, they are in suspension in water.

BSPR:

The preparation of the polishing baths is carried out simply by the addition of the composition of the invention, in powder form, to the aqueous medium which is agitated manually or by conventional agitating means (anchor, helical, turbine agitators, or the like) or are used as such if the composition of the invention is in the form of an aqueous suspension.

BSPR:

The amount of water used in the preparation of the polishing bath is not critical, but it is preferable, in order to impart good maintenance in suspension of the composition of the invention, to use a soft water, i.e., a water having a hardness of less than 5.degree..TH.

BSPR:

It may be advantageous to add to the polishing bath an antifoaming agent, such as, for example, a polysiloxane. The amount of such agent may constitute from 0.1 to 10% by weight of the composition of the invention.

BSPR:

The temperature of the bath is selected such that it is less than 30.degree. C. It is advantageous to utilize lower temperatures, ranging from 1.degree. to 10.degree. C., as any increase in temperature decreases polishing efficiency.

BSPR:

The polishing compositions of the invention offer numerous advantages:

BSPR:

(b) they provide an improved performance: very good polishing

efficiency, as high as that attained with alumina and, thus, rapid polishing (a time advantage of up to 50% relative to that required using ceric oxide alone), as well as very low rates of rejection of the polished final articles;

BSPR:

In the examples to follow of the compositions of the invention for the polishing of organic glasses, the following polishing test was employed to evaluate their performance:

BSPR:

These were configured as spherical rollers having a diameter of 70 mm, only the concave face (concavity=-6 diopters) of which was subjected to the polishing operation. The other face surface, which was not polished, was coated with a flat black paint to protect said surface and to facilitate the observation of the resulting polish.

BSPR:

In view of their fragility and sensitivity to scratching, organic glasses require preparation: clear polishing, which consists of preparing the surface of the roller and to provide a reproducible surface in order to subsequently quantify the material removed during the polishing operation.

BSPR:

1. The clear-polishing tests were carried out on a COBURN 603 single spindle machine, the polishing element of which was sprayed uniformly with water.

BSPR:

The abrasive polishing agent was changed after each test.

BSPR:

2. The polishing efficiency of the compositions of the invention was measured in the following manner:

BSPR:

The polishing tests were carried out on a COBURN 603 machine having a single spindle, the polishing element of which was a flocked velour, and it was sprayed uniformly with the composition to be tested.

BSPR:

Prior to performing the polishing efficiency measurements, the machine was adjusted using a standard product.

BSPR:

The polishing efficiency is expressed as the average of 3 tests.

BSPR:

3. The very nature of the substrate requires that the polishing of organic glasses be discussed in terms of efficiency combined with the quality of the polish.

BSPR:

The condition of the surface was observed immediately following polishing, while avoiding any mechanical pressure on the surface, particularly during the rinsing with deionized water and drying with compressed air.

BSPR:

Examples 1 to 4 describe the polishing compositions which subsequently were tested for the polishing of organic glass, such as described in Example 5.

BSPR:

Examples 6 to 8 illustrate, relative to the preceding examples, different polishing compositions, using either another source of ceric oxide (Example 6) or a different cerous oxide (Examples 7 and 8) and their use in the polishing of organic glass.

BSPV:

(vi) Polishing agent: abrasive (UNIVERSAL MF 10)

BSPV:

(vii) Polishing element: flocked velour (ALPHA LAP)

BSPV:

(ii) with a magnifying glass, to detect finer cracks and grain. These would indicate an insufficient polishing time, as it is due to a clear-polishing residue;

BSPV:

(iii) with a light condenser. The light beam impacts the surface in a glancing manner and makes it possible to observe streaks, and particularly the presence of hazing after polishing.

DEPR:

In this example, the polishing composition was prepared in the powder form.

DEPR:

The mixture was then directly placed in suspension in deionized water, in the concentration required for polishing, i.e., 400 g/l (expressed as CeO₂ sub.2).

DEPR:

In the following example, the polishing composition was produced by impregnation.

DEPR:

The mixture was then placed in suspension directly in deionized water, in the concentration required for polishing, i.e., 400 g/l (expressed as CeO₂ sub.2).

DEPR:

The compositions described in Examples 1 to 4 were used in a polishing test carried out under the aforementioned conditions.

DEPR:

As a comparison, in Table II the polishing efficiency of polishing compositions having the compositions of Examples 1 to 4, but with the cerous salt omitted, is reported:

DEPR:

The polishing efficiency which was realized using the foregoing composition was 56 mg/dm² /min.

DEPR:

The polishing efficiency which was realized using the aforementioned polishing composition was 48 mg/dm² /min.

DEPR:

The polishing efficiency which was realized using this polishing composition was 49 mg/dm² /min.

DEPR:

The organic glass displayed no cracks or surface hazing after polishing.

DETL:

TABLE I mg/dm² /min Quality of polish Polishing efficiency in Example 1 55 .+-. 5 no cracks no haze on surface Example 2 50 .+-. 5 no cracks no haze on surface Example 3 55 .+-. 5 no cracks no haze on surface Example 4 55 .+-. 5 no cracks no haze on surface

DETL:

TABLE II mg/dm.sup.2 /min	Quality of polish	Polishing efficiency in Test A 25 fine cracks - surface haze Test B 20 fine cracks - surface haze Test C 25 fine cracks - surface haze Test D 25 fine cracks - surface haze
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CLPR:

1. A cerium-based composition of matter adapted for the polishing of organic glass surfaces, comprising intimate admixture of particulate ceric oxide and at least 0.2% by weight of a water soluble cerous (III) salt based on the weight of ceric oxide.

CLPR:

3. The cerium-based composition a defined by claim 1, said particulate ceric oxide comprising a powder having particle sizes less than about 20 .mu.m.

CLPR:

4. The cerium-based composition as defined by claim 3, said powder having particle sizes ranging from about 0.1 .mu.m to 10 .mu.m.

CLPR:

28. In a method for the polishing of an organic glass surface utilizing an abrasive polishing agent, the improvement which comprises, as the polishing agent therefor, the cerium-based composition as defined by claim 1.

CLPR:

29. In a method for the polishing of an organic glass surface utilizing an abrasive polishing agent, the improvement which comprises, as the polishing agent therefor, the aqueous suspension as defined by claim 25.

CLPR:

30. The polishing method as defined by claim 29, said organic glass surface comprising a plastic ophthalmic lens.

CLPR:

31. The polishing method as defined by claim 29, said organic glass surface comprising a plastic sheet material.

CCOR:

106/3

CCXR:

51/308

CCXR:

51/309

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